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Chemical Technology and Economics in Environmental Perspectives. Task I

Midwest Research Institute

Prepared For
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February 1976

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CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVES

TASK 1-TECHNICAL ALTERNATIVES TO SELECTED CHLOROFLUOROCARBON USES

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ENVIRONMENTAL PROTECTION AGENCY
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16. ABSTRACT

The purpose of this study was to identify technically feasible substitute chemicals and/or alternative methods of delivering the goods and services presently provided through the use of the five commercial chlorofluorocarbons FC-11, -12, -13, -113, and -114. This study did not involve an assessment of the risks associated with environmental discharge of these chemicals. For the purposes of this study, recovery and/or recycling were not to be considered as eligible alternatives. Four categories currently account for 99% of the usage of these compounds. These areas are: refrigeration and air conditioning, aerosol propellants, plastic foam blowing agents, and cleaning and drying applications. In addition to these four areas, the Rankine Cycle engine was considered as it appears to have potential for expanding future consumption of chlorofluorocarbons. Limited evaluations were made on the direct economic consequences which could result from a reduction or elimination of chlorofluorocarbon consumption in each of the current use areas.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Task I - Technical Alternatives to Selected Chlorofluorocarbon Uses

Contract No. 68-01-3201

Project Officer
Irving J. Gruntfest

Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

Prepared for

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Office of Toxic Substances
Washington, D.C. 20460

February 1976

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PREFACE

This report presents the results of Task I, "Technical Alternatives to Selected Chlorofluorocarbon Uses," of a project entitled "Chemical Technology and Economics in Environmental Perspectives." The project is performed by Midwest Research Institute (MRI) under Contract No. 68-01-3201 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Dr. Irving J. Gruntfest is the project officer. This program has MRI Project No. 4101-C.

Particular credits for authorship of portions of this report include the following: Mr. G. J. Hennon, Chapters III and VIII-A; Ms. Kathryn Lawrence, Chapters IV, VI-B, and VIII-B; Mr. Howard Gadberry, Chapter V; Dr. Roderick E. Athey, Chapter VII; Dr. Ivan C. Smith and Dr. Thomas W. Lapp, Chapters II, VI-A, and VIII-C,D. Ms. Cassandra Collins provided technical assistance for portions of this study. Dr. Lapp is the project leader for this contract. This program is under the supervision of Dr. Edward W. Lawless, Head, Technology Assessment Section, Physical Sciences Division.

MRI expresses its sincere appreciation to the many companies and organizations that provided technical information for this report.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon

L. J. Shannon, Assistant Director
Physical Sciences Division

March 11, 1976

PREFACE

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MIDWEST RESEARCH INSTITUTE

L. J. Shannon

L. J. Shannon, Assistant Director
Physical Sciences Division

March 11, 1976

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I. INTRODUCTION

The technical controversy over whether certain chlorofluorocarbons are destroying the earth's protective ozone shield has evolved into a public issue. Legislation is being considered at both the state and federal levels to limit or ban the use of certain of these materials. One state, Oregon, has banned the use of chlorofluorocarbons in aerosol sprays. While many technical questions remain to be answered, responsible public officials and regulatory agencies are trying to determine the technical and economic feasibility of using alternative chemicals, or of substituting mechanical devices where suspect chlorofluorocarbons are now used. In addition, they seek to identify the social consequences resulting from the regulation of the various uses of these materials.

There have been numerous articles in the press referring to the ozone problem and to the effects of "fluorocarbons" on the depletion of the ozone layer. In actuality, the problem is not specifically fluorocarbons but rather the highly halogenated chlorofluorocarbons or bromofluorocarbons. The term "Freons" has also been widely used in the press as being synonymous with fluorocarbons, which of course it is not since the term Freon® is the registered tradename of E. I. du Pont de Nemours and Company.

It should also be noted that not all chlorofluorocarbons or fluorocarbons are considered to be equally detrimental to the ozone layer nor are these compounds the only halogenated species in the upper atmosphere. In very simplified terms, the current controversy lies in the mechanism and relative rates of chlorine and fluorine atom (free radical) reaction with ozone. In the upper atmosphere, the halogenated species undergoes photodissociation to produce halogen atoms (free radicals), which in turn react with ozone. Originally it was thought that the chlorine reacted with ozone at a rate 10 times faster than fluorine. The five halocarbons covered in this report are considered to be the most potentially hazardous of the commercially produced chlorofluorocarbons. Other commercially available chlorofluorocarbons are, at this time, considered to be less hazardous to the ozone layer and, in fact, some of these materials have been suggested in this report as possible alternative materials.

Previous studies on chlorofluorocarbons have dealt with stratospheric effects, biological effects of ozone reduction, human health effects, and a review of the "fluorocarbon industry."[1] A study conducted by Syracuse University Research Corporation offered an appraisal of environmental hazards of one and two carbon fluorocarbons.[2] Another major study was a preliminary impact-assessment of possible regulatory actions to control atmospheric emission of selected halocarbons.[3] It covered 24 halocarbons and identified the major emission sources of those compounds, analyzed alternatives for emission abatement, named the affected industries, and assessed economic impacts of regulatory options. Reports on other studies by the Department of Commerce on the economic and energy impacts of chlorofluorocarbon regulation were not received in time for use on this program.

The objective of this study is to explore more deeply than have any previous studies, the technical feasibility of and the basic economic considerations related to use of alternative chemicals or mechanical devices for supplying the public with the same goods and services now provided by five of the most potentially hazardous halocarbons: chlorofluorocarbons 11 (CCl_3F), 12 (CCl_2F_2), 13 ($CClF_3$), 113 (CCl_2FCClF_2), and 114 ($CClF_2CClF_2$).

This study was not directly concerned with the current ozone depletion hypothesis or the environmental ramifications of that hypothesis. No judgment on that question should be inferred from any of the results of this study.

Four major-use categories (aerosols, refrigerants, solvents, and foam-blowing agents) account for over 99% of the usage of these five materials. Working closely with industry, MRI has appraised the various substitute chemicals or alternative mechanical devices available in each of the use areas, should the five chlorofluorocarbons be banned from further use. Recovery of these chemicals, although a plausible solution for some emission problems was not to be considered a viable solution in this study. Costs while of intense concern to the consumer, were not used to exclude technologically feasible alternative systems from further consideration in this study. Willingness of the public, once informed of the risks, to forego certain conveniences afforded by these chemicals, should not be underestimated, as evidenced by the 25% reduction in sales of chlorofluorocarbon propelled aerosols over the last few months. The following sections of this report contain a discussion of technical feasibility for the use of the alternatives in each of the four use categories.

This document is intended to be useful to policy makers and the public in understanding the technical difficulties associated with the development of acceptable substitutes for these five materials if or when their use should be limited. It is organized in a manner which we feel will provide the greatest utility to the reader. The next section summarizes the findings of this study and presents conclusions with respect to the utilization of alternative systems for each of the four present use areas of the selected chlorofluorocarbons. Sections III through VI present a detailed discussion of the technical considerations to be applied to alternative systems in the areas of refrigeration and air conditioning, aerosols, foam-blowing applications, and degreasing and dry cleaning solvents. For each of these areas, a range of alternatives are shown but no attempt has been made to select the single most attractive alternative or to provide any rank-order of the alternatives. Section VII is concerned with a possible major future use of chlorofluorocarbons, (i.e., in the Rankine Cycle engine) and with the numerous alternatives which may be possible in this use area. Section VIII presents a brief summary of some economic considerations for the use of various alternative systems in each of the four areas discussed in Sections III through VI.

Throughout the literature and in discussions with personnel directly involved with the industry, several different designation systems are widely used for the halocarbons. In all industries, other than refrigeration, the halocarbons are given an F prefix (fluorocarbon) while in the refrigeration industry the compounds have an R prefix (refrigerant). In some instances, the designation "P" is also used to denote an aerosol propellant but finds very limited usage. Thus, F-12 and R-12 are the same compound, only the prefix has been changed to reflect the views of two different industries. In addition, certain company trademark names such as Freon® (E. I. du Pont de Nemours and Company), and others are used.

Information was received from a major manufacturer immediately prior to the printing of this final report regarding two of the compounds (F-21 and F-115) suggested as possible alternative materials. Current legislative attitudes indicate that any chlorofluorocarbons not containing hydrogen or a carbon-carbon double bond may be restricted in the future. If this materializes, F-115 would be included in such action and would not be acceptable as an alternative. Recent toxicological data on F-21 indicates that the material probably is not acceptable as an aerosol propellant. Since this information became available at a time which made the deletion of these two compounds from the report impractical, references to these materials do remain in the report. However, any suggested use of F-21 and/or F-115 in this report should be modified in view of the above comments.

REFERENCES TO SECTION I

1. "Fluorocarbons and the Environment," Report of Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS), Council of Environmental Quality, June 1975; GPO No. 038-000-00226-1.

2. Howard, P. H., P. R. Durkin, and A. Hanchett, "Environmental Hazard Assessment of One and Two Carbon Fluorocarbons," EPA Contract No. 68-01-2202, Technical Report TR-74-572 (1974); EPA Report No. 560/2-75-003; NTIS No. PB-247-419.

3. Arthur D. Little, Inc., "Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons," EPA Contract No. 68-02-1349, Task 8, Publication No. EPA-450/3-75-073, September 1975; NTIS No. PB-247-115.

II. SUMMARY AND CONCLUSIONS

The chlorofluorocarbons are a unique class of chemicals, many of which are chemically very unreactive, nearly odorless, and generally nontoxic and nonflammable. Because of these properties and the desirable boiling points, vapor pressure characteristics and solvent properties exhibited by certain chlorofluorocarbons, they are in demand for a broad range of domestic and industrial uses and are manufactured in quantities of millions of pounds. The higher costs of these compounds, compared to those of available substitute chemicals has been accepted by the public in preference because they pose lower health risks and afford greater convenience in certain applications.

The purpose of this study was to identify technically feasible substitute chemicals and/or alternative methods of delivering the goods and services now provided through the use of suspect chlorofluorocarbons. This study did not involve an assessment of the risks associated with environmental discharge of these commercially important chemicals. While cost was not a primary consideration in selecting substitute chemicals and/or alternative methods of delivering a good or service, it was not ignored in this study. This study was limited to the five commercial compounds believed to pose the greatest environmental threat (F-11, F-12, F-13, F-113 and F-114), if the current ozone depletion hypothesis is found to be correct.

It has recently been stated in a governmental report that four categories currently account for 99% of the usage of these compounds (Table II-1).

Thus, the focus of this study is on those four use categories. The Rankine Cycle engine is an application which appears to have considerable potential for expanding future usage of chlorofluorocarbons. Alternative chemicals for this application are discussed.

The results of this study can be summarized as follows for each use category.

A. Aerosols

Chlorofluorocarbons F-11 and F-12 account for over 92% of the chlorofluorocarbons used in the aerosol industry. Fluorocarbon-propelled products are widely used by the public as convenience items (convenience for which they are willing to pay). However some products would not be on the market if aerosols were not available. Similar goods or services can

TABLE II-1

PRODUCTION AND MAJOR USES OF CHLOROFLUOROCARBONS (1972)[a]

Compound	Sales[b]	Production	Aerosol Propellants	Refrigerants	Solvents[c]	Foaming Agents[c]
F-11	285	300	215	19	5	50
F-12	415	439	220	132		45
F-13	Very small	NA		Very small		
F-113		50			50	
F-114	—	20	20	10	—	—
	700	809	451	161	55	95

---

[a] In millions of pounds.

[b] Sales 5% less than production because of inventory buildups.

[c] No authoritative data are available regarding the precise quantities used for various applications or the compound used. Estimates shown throughout this report may vary according to the sources.

Source: "Fluorocarbons and the Environment," Report of Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS), Council on Environmental Quality and Federal Council for Science and Technology, 1975.

often be provided without chlorofluorocarbons. Sales of chlorofluorocarbon-propelled aerosols have significantly diminished during the past few months. This reduction in sales can be attributed for the most part to the economic recession and is also partly indicative of the public's concern about potential environmental hazards of these materials, and indicates a willingness to accept alternate products in some categories. It also reflects the technical and marketing efforts of some manufacturers of aerosol products.

In this study, potential substitute propellants or alternative methods of delivering current aerosol products are identified and evaluated. Aerosol application of chlorofluorocarbons are shown to fall into three categories: (a) personal products, (b) household products, and (c) other products.

Personal products account for about 84% of the chlorofluorocarbon propellants used in aerosols: hair care, antiperspirants and deodorants account for 90% of that usage. Low flammability, low toxicity, and absence of objectionable odor are important criteria for alternative candidates to meet in these applications. Alternatives identified include other chlorofluorocarbons, hydrocarbons, compressed gases and mechanical devices.

Other chlorofluorocarbons that could be used as alternatives to the F-11 and F-12 in such products include F-115,* FC-318, F-21,** F-22, F-142b and F-152a. Candidates still in the experimental stage include: F-123, F-124, F-132b, and F-133a. F-218, F-227a and F-3110 would require a longer time period for development and implementation. Most of these materials could be as much as 5 to 10 times more expensive than F-11 or F-12.

Hydrocarbons afford the necessary performance features and are much less expensive; however, their high flammability will deter their usage for this purpose, unless suitable flammability suppressants can be found. Shaving lathers are largely propelled by hydrocarbons already, and could be converted entirely to these propellants with little problems.

Compressed gases such as nitrogen, carbon dioxide, and nitrous oxide will require larger cans for the same net weight of product and lower proportions of active product. Industry advances in nozzle design and incorporation of various mechanical features (bladder systems, pistons, etc.) may allow substitution of compressed gases for some uses of chlorofluorocarbons if the market is willing to accept some tradedown in using these systems. Mechanical substitutes appear to be feasible and acceptable alternatives for delivery of some personal care products (hair sprays, most medicinals, pharmaceuticals, colognes and perfumes).

---

* Industrial sources recently indicated that F-115 may not be an acceptable substitute because it contains only chlorine and fluorine, as such, may be restricted in future legislation.

** A major manufacturer states that recent toxicological data indicate that F-21 probably is not acceptable as an aerosol propellant.

Household products such as room deodorants, cleaners, laundry products and waxes and polishes account for only 6% of the chlorofluorocarbon-propellant usage in aerosols. In household applications, about 80% of the aerosol propellants are hydrocarbons. Some chlorofluorocarbons, hydrocarbons, and compressed gases could be substituted for the small usage of F-11 and F-12 in these aerosol applications. However, some increased consumer costs and/or hazards associated with the chemical alternatives could preclude extensive substitution in aerosol products where they are now used. Mechanical delivery systems, already widely used for these products, appear to be acceptable alternatives.

Other products delivered with chlorofluorocarbon propellants account for about 10% of all chlorofluorocarbon-propelled products. These products consist predominantly of pesticides, coatings (e.g., paints), and industrial products. Hydrocarbons are now the most widely used propellants for these products, and could almost entirely replace the chlorofluorocarbons for these uses. The more expensive chlorofluorocarbons F-115 and FC-318 have been and are currently used (in relatively small total amounts) in combination with N_2O in some food products such as whipped cream. Mechanical delivery systems are also available for most products in this category.

B. Refrigeration

Mechanical vapor-compression systems (MVCS) are used for both refrigeration and air conditioning, and account for the vast majority of the refrigerating capability in the U.S. While sulfur dioxide and ammonia were once used as the refrigerants in these systems, chlorofluorocarbons are now used almost exclusively, because of their much lower toxicity and nonflammability as compared to ammonia. However, ammonia is still used in some commercial applications. If the use of F-11, F-12, and F-114 as refrigerants were to be banned two alternative approaches are available: (a) employ other working fluids in MVC refrigeration, or (b) substitute other refrigeration systems for MVC.

1. Chemical substitutes: Flammability, toxicity, chemical stability and thermodynamic properties are primary considerations in selecting refrigerant fluids. Chemicals having the necessary physical and thermodynamic properties have been identified and evaluated. The 1972 ASHRAE Handbook of Fundamentals lists 78 potential refrigerants, including the chlorofluorocarbons. At present, F-11, F-12, and F-114 account for over 65% of the working fluids used in MVC systems. One additional chlorofluorocarbon, F-22, is also used extensively as a refrigerant, and could replace F-11 and F-12 in many applications but only with substantial redesign of refrigeration systems. Redesign and retooling would be expensive and industry is showing a considerable reluctance to redesign or retool to use F-22 as a refrigerant until they are assured that it too will not be banned.

While many other chemicals may be technically feasible alternative refrigerants, few of them are near-term candidates, either because their physical and chemical properties are not suitable or are undetermined, adequate production capabilities are not available or production costs would be very high. Many of them would probably not be allowed for use in the home because of their toxicity or flammability, and Occupational Safety and Health officials may restrict their use in the industrial workplace for the same reasons.

2. Alternative refrigeration systems: Alternative refrigeration systems could be used in place of F-11 and F-12 mechanical vapor compression systems for some applications. The lithium bromide absorption system, while less efficient than MVC, could be used in air conditioning and chilling applications.

Ammonia-absorption systems could be used for low temperature applications, but have the same drawbacks as ammonia-MVC (i.e., toxicity and explosiveness).

Thermoelectric cooling is far too expensive except for a few specialized applications.

Steam-jet refrigeration has limited potential as a substitute refrigeration system for a few industrial applications.

The air cycle, although showing some potential as a long-term substitute, has little or no short-term capabilities as a replacement refrigeration system.

C. Foam Blowing Agents

Approximately 78 million pounds of chlorofluorocarbons were used in 1974 for the fabrication of plastic foams. This application accounts for about 8% of U.S. chlorofluorocarbon usage.

By far the largest usage of chlorofluorocarbon blowing agents is in the manufacture of rigid polyurethane foams--mainly for thermal insulation. Nearly 46 million pounds of F-11, F-12 and other chlorofluorocarbons are used annually for rigid urethanes. Because a substantial portion of the chlorofluorocarbon vapors are trapped within the closed cells of rigid urethane foams, emissions to the atmosphere are significantly lower than annual consumption. Total cumulative emissions of chlorofluorocarbons to the atmosphere since 1965 from all types of plastic foams is estimated to be 256 million pounds, or roughly one half of the 483 million pounds estimated cumulative consumption in foam blowing.

Flexible urethane foams are the second largest user of chlorofluorocarbon blowing agents. Current consumption for flexible urethanes is about 23 million pounds. Chlorofluorocarbons are used to augment blowing from the carbon dioxide released by reaction of free isocyanate groups with water. The addition of chlorofluorocarbons as auxiliary blowing agents improves the softness of the foams and reduces hysteresis. Virtually all of the chlorofluorocarbons used in preparing flexible foams is lost to the atmosphere soon after manufacture. A few other plastic foams consume small quantities of chlorofluorocarbons, although most other foams employ other means of foam generation. Polystyrene foamed sheet and film prepared from crystal consume nearly 7 million pounds of chlorofluorocarbons. Polyethylene foams account for about 1 million pounds of F-114, F-11, and F-12. Because other blowing agents (such as pentanes or methylchloride) can also be used to prepare styrene and olefin foams, only about 5% of styrene beads and extruded board stock use any chlorofluorocarbon, but 40 to 45% of foamed styrene sheet is chlorofluorocarbon blown. Virtually all chlorofluorocarbons used in styrene, olefin, and miscellaneous foams diffuse promptly into the atmosphere.

The distribution of chlorofluorocarbons used in plastic foams is not known with accuracy. One major producer of foams estimated the distribution for 1973 to be:

F-11	53 million pounds
F-12	10 million pounds
F-113	~ 2 million pounds
F-114	~ 3 million pounds
Total	~ 68 million pounds

Fluorocarbon producers indicate that while the distribution given is reasonable, total consumption is probably 20 million pounds greater. The major difference is believed to lie in substantially higher use of F-12, which has grown quite rapidly in recent years.

Blowing agents represent a relatively small part of the total cost of plastic foams. At current prices the nearly 78 million pounds used in 1973 cost about $30 to $35 million; or roughly 4 to 6% of the cost of raw ingredients for foam products.

At present, chlorofluorocarbons are considered essential in achieving the low thermal conductivity required for insulating foams. Because low density foams (2 lb/cu ft) consist of about 97% vapor within the cells and 3% actual polymer, it is the thermal conductivity of the cell gases that determines the overall K-value. While a few other vapors (mostly halogenated compounds) are known that compare with the low thermal conductivity of the chlorofluorocarbons, these agents are not used in preparing insulating foams. It is conceivable that compounds other than the chlorofluorocarbons now used almost totally for insulating foams could be developed for use as auxiliary blowing agents, but to date no satisfactory substitute has been found. The cost of possible alternative blowing agents could be lower than or higher than the chlorofluorocarbons that are used at present. If all of the 78 million pounds of chlorofluorocarbons used for foams were eventually replaced by alternative blowing agents costing 80¢/lb more (roughly three times present prices), the increased cost would total $62 million. For the present annual output of 898 million pounds for all types of fluorocarbon-blown foams, the added cost to the user would amount to about 7.0¢/lb of foam. If chlorofluorocarbon usage in thermal insulating foams were curtailed, foam usage in building construction, refrigeration appliances, and industrial applications would be affected markedly. The froth-pouring and froth-spraying techniques which are growing in usage are believed to depend on the use of F-12 to preexpand the plastic froth. Because foamed insulation is currently quite cost-effective (especially for the application of insulation to already existing structures and equipment), elimination of foamed insulation could inhibit efforts toward energy conservation.

Chlorofluorocarbon blowing agents are also considered essential in preparing soft flexible urethane foams. Without the use of auxiliary blowing agents, flexible urethanes do not provide the cushioning characteristics on which most automotive seating and some furniture applications are based. The use of chlorofluorocarbons may also be required at present in making super-soft foams for textile lamination, and for self-bonded rug backings.

A wide variety of other materials compete with plastic foams for most applications. In fact, most of the present uses of plastic foams represents a displacement by the foams of some material formerly used for the same purpose. Substitution of alternate materials would be possible for many products and applications now consuming plastic foams. In many cases, such substitution would mean less satisfactory or more costly products. For certain major uses of plastic foams, there is no presently available substitute.

While it might be practical to develop systems to collect, purify and reuse chlorofluorocarbons lost during plastic foam production in plants, no proven system now exists for chlorofluorocarbon recovery.

D. Cleaning and Drying Solvents

These applications represent areas in which the chlorofluorocarbons play a relatively minor role both with respect to the total quantity of solvents used and to the overall consumption of chlorofluorocarbons among the four use areas. The consumption of F-113 and F-11 represents only approximately 6% of the total solvents used for cleaning and only about 9% of the total production of the five chlorofluorocarbons.

The use of F-113 and F-11 in the cleaning field is concentrated in the electrical and electronics industries for the defluxing of printed circuit boards (PCB's) and the cleaning of electronic parts, electric motors, and delicate electronic and scientific instruments. The solvents are also used to clean metal, glass, plastics, and electroplated manufactured articles. A dry-cleaning process compatible with plastic buttons and trim, furs, and leathers has been commercialized. F-113 and F-11 based cutting fluids are widely used in industries such as aircraft construction where precise tolerances must be maintained.

F-113 based displacement drying fluids are used to remove water from metal, glass, plastic or plated parts to leave a spotless, residue-free surface.

Designation of suitable alternatives for the current uses of F-113 and F-11 is difficult since each cleaning or drying problem is unique. Factors that would influence the selection of a specific solvent are:

* Type of soil and/or grease to be removed--ionic, nonionic or both, particulate matter.
* Compatibility of the object cleaned or dried with the solvent.
* Temperature limits of the objects to be treated.
* Solvent flammability.
* Employee safety vis-a-vis solvent exposure--toxicity, TLV OSHA regulations, effect on skin, and eyes.
* MIL Specifications governing choice of solvent and cleanliness tests for the finished article.
* Solubility in water.
* Energy requirements.
* Reject rates.
* Waste disposal.
* Cost/unit object cleaned or dried.

In theory, the existing chlorocarbons, aqueous detergent or cleaner systems and flammable solvents could be potential substitutes for some of the current applications of F-113 and F-11. The chlorocarbons to be considered as possible substitutes would include perchloroethylene, methylene chloride, methyl chloroform, and trichloroethylene. Flammable solvents that may have some application include alcohols, ketones, and hydrocarbons; however, the use of these solvents would not be recommended for more general usage unless they are used in very small quantities under very controlled conditions. Regardless of the alternative solvent, certain tradeoffs will occur among the various factors stated earlier and the ultimate alternative should represent the most viable material with respect to overall system efficiency, worker safety, environmental effects, and other direct concerns.

As a dry-cleaning agent, F-113 is used primarily for specialty cleaning with only very minor usage in other areas. Other currently used dry-cleaning solvents, such as Stoddard solvent or perchloroethylene, can be used as substitutes for the cleaning of these specialty items.

To reiterate an earlier statement, the designation of suitable alternatives for the current uses of chlorofluorocarbon cleaning and drying agents is difficult since each problem is unique. The potential of a possible substitute must be considered on a case-by-case basis considering the relative advantages and disadvantages of each solvent.

III. REFRIGERATION AND AIR CONDITIONING

This section of the report addresses the technological considerations for using alternative chemical and/or mechanical substitutes for selected chlorofluorocarbons in refrigeration and air conditioning.

General considerations in choosing a refrigeration system can be summarized as follows: (a) is the system technically capable of operating in the temperature and humidity range necessary for the contemplated end uses ("engineered refrigeration systems may have as a target any dry-bulb temperature from +70°F (+21°C) down to -240°F (-151°C), and relative humidities from 95 to 0%, or combinations of dry-bulb and humidity control"1/); (b) is the system adaptable to the physical size limitations of the end-use product; (c) is the system economically feasible in terms of initial investment and operating costs; and (d) is the system safe to use in the desired application?

The report discusses chlorofluorocarbon systems for refrigeration and air conditioning, describes alternatives to the chlorofluorocarbons under study, and describes the applicability of alternatives in specific use areas.

A. Chlorofluorocarbon Systems for Refrigeration and Air Conditioning

Chlorofluorocarbons are used in mechanical vapor compression refrigeration and air conditioning applications. A breakdown by end-use products is shown in Table III-1. Inasmuch as this program is primarily concerned with alternatives for R-11, R-12, R-13, R-113 and R-114,* the use breakdown translates to the fact that R-11 and R-12 account for more than 88% (Table III-2) of refrigerant usage for the five chlorofluorocarbons under study. Accordingly, the largest portion of effort in this part of the study has dealt with possible alternatives to R-11 and R-12 refrigerant systems.

1. Mechanical vapor compression systems: The ASHRAE Guide and Data Book provides detailed descriptions of reciprocating, rotary, and centrifugal type compressors. Very simply stated, the following actions take place in these systems: (a) a refrigerant vapor is compressed, thereby raising its temperature and pressure; (b) the high-pressure (warm) gas is then condensed to a high pressure (warm) liquid and heat is dissipated from the condensor; (c) the high-pressure liquid is pumped through a metering device and into an evaporator where it vaporizes to a low pressure (cool) gas extracting heat from the surroundings and producing the refrigeration effect; and (d) the low-pressure gas is returned to the compressor for recycle.

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* The "R" designation is standard industry terminology for "refrigerant" and, for the chlorofluorocarbons, replaces the "F" designation used in other industries.

TABLE III-1

CHLOROFLUOROCARBON USE AS REFRIGERANTS BY END-USE PRODUCTS

Type of Equipment	Refrigerant Commonly Used	Unit Estimates				
		Units in Service (millions)	Units Shipped 1973 (millions)	Units Scrapped 1973 (millions)	Average Unit Charge (lb/unit)	Original Charge 1973 (million lb)
Major Appliances						
Room A/C[a]	22	29.0	5.35	4.00	2.00	10.7
Dehumidifiers[a]	12	5.1	0.65	0.16	0.84	0.5
Freezers[a]	12	22.4	2.42	1.10	1.25	3.0
Refrigerators[a]	12	68.7	6.77	4.00	0.63	4.3
Other						
Ice Makers[a]	12	1.3	0.22	0.03	2.00	0.4
Water Coolers[a]	12	3.8	0.39	0.16	1.00	0.4
Mobile A/C[b]	12	45.0	7.53	7.00	3.80	28.6
Unitary Residential A/C[c]	22	11.4	2.15	0.40	4.5	19.8
Unitary Commercial A/C[c]	22	4.0	0.62	0.17	36.0	22.3
Centrifugal Chillers[d]	11,12,22	0.05	0.005	0.001	2,500.0	12.5
Reciprocating Chillers[c]	11,12,22	0.2	0.02	0.003	350.0	7.0
Unit Coolers[a]	12	1.7	0.19	0.12	14.0	2.7
Food Store Refrig.[d,e]	12,22	0.2	0.008	0.006	675.0	5.4
Mobile Refrig.[c]	12	0.5	0.07	0.03	14.0	1.0
Beverage Refrig.[c]	12	23.8	3.57	0.65	1.2	4.3
Packaged Terminal A/C[a]	22	1.0	0.15	0.03	2.5	0.4
Other	-	-	-	-	-	9.0
Total	-	-	-	-	-	132.3

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[a] Factory-charged sealed units.
[b] Mobil (automobile) air conditioning unit.
[c] Field-charged sealed compressor units.
[d] Field-charged open motor units.
[e] Unit data are on a per store basis.
Source: Arthur D. Little Report[2] and a major manufacturer.

TABLE III-2

ESTIMATED CHLOROFLUOROCARBON USE AS REFRIGERANTS

Chlorofluorocarbon	1973 End Use million lb	1973 End Use %
R-11	18	6
R-12	168	56
R-22	90	30
Other	24	8
Total	300	100

Note: If R-22 is eliminated from the above table and the 8% in the "other" category is assumed to be all R-13, R-113 and R-114, then R-11 and R-12 are calculated to account for a minimum of 88.6% of the five chlorofluorocarbons under study. Ten million pounds of R-114 was used as a refrigerant in 1972,[3] which, on the basis of the above table, would account for an additional 3.3%.

Source: Arthur D. Little Report.[2]

a. Reciprocating compressors: Reciprocating compressors (those in which a piston travels back and forth in a cylinder) are presently used in applications up to approximately 100 tons refrigeration capacity. This upper limit is due to considerations of reliability, life expectancy, and energy consumption. Generally, these systems use R-22 for comfort air conditioning applications (evaporator temperatures of 40 to 50°F (4 to 10°C))[1] and R-12 or R-502 (azeotrope of R-22 and R-115) for lower temperature applications. End use products utilizing reciprocating compressors and essentially 100% R-22 include room air conditioners, unitary residential air conditioners, unitary commerical air conditioners, and packaged terminal air conditioners. Other reciprocating compressors utilizing R-22 are used in chillers and food store refrigeration. Reciprocating compressors using essentially 100% R-12 or R-500 include dehumidifiers, home freezers and refrigerators, ice-makers, water coolers, unit coolers, mobile refrigeration, and mobile air conditioners.[1,4] (mobile denotes automobile and light trucks up to 10,000 lb GVW).[5] Other reciprocating compressors utilizing R-12 are used in chillers and food storage refrigeration. For reciprocating compressor applications, this study is primarily concerned with the latter group of end-use products which use the R-12 refrigerant.

b. Rotary compressors: Rotary compressors (those in which an eccentric rotates within a cylinder) are used for fractional tonnage applications in some appliances. Most of these units operate on R-12 refrigerant. R-114 can be used in rotary compressors for small appliances. Helical rotary compressors can be obtained in 120 to 350 ton capacity.[1]

c. Centrifugal compressors: Centrifugal compressors (those in which an impeller, rotating within a housing, draws in vapor and discharges it at high velocity by centrifugal force) are usually broken into three capacity ranges: lower capacity, 100 to 1,500 tons, commonly use R-11; intermediate capacity, 1,000 to 6,000 tons, commonly use R-12 or sometimes R-114; higher capacity, 5,000 to 15,000 tons, commonly use R-22.[4] R-113 can be used in systems above 50 ton capacity.[6] The practical upper limit of capacity of centrifugal compressors is determined only by physical size.[1] Centrifugal units are used to cool a secondary refrigerant, such as water or brine, which is then circulated to cool large enclosures. In practice, R-22 is rarely used in centrifugal chillers because of the high operating pressures. The chiller market, excluding absorption systems, is approximately two-thirds R-11 and one-third R-12 and R-500 (azeotrope of R-12 and R-152a).[7]

2. Physical and chemical characteristics of mechanical vapor compression working fluids: "The choice of the refrigerant for a particular application often depends on properties not directly related to its ability to remove heat. . . .As a rule, the selection of a refrigerant is a compromise between conflicting desirable properties."[1] There are but a very few truly technical limitations in selecting materials for use as refrigerants.

"Anything is technically feasible if energy and cost are not considered factors."[8] "It is technically feasible to utilize nearly any organic compound as a refrigerant."[9] However, there are technical limitations on which materials can be used in a given temperature range:[1] (a) the boiling point of a refrigerant indicates directly the general temperature range within which a refrigerant can be used; (b) the freezing point of a refrigerant must be lower than any contemplated usage; and (c) in refrigeration cycles involving condensation, a refrigerant must be chosen so that the condensation will occur at a temperature somewhat below the critical temperature (temperature above which a vapor cannot be condensed).[1]

In reality a great many factors influence the choice of a chemical compound for use as a refrigerant. The following considerations have been stated and are presented not necessarily in order of importance:

Property Chemical and Physical	Reason for Consideration
Boiling point	Determines temperature application range.
Critical temperature	Determines upper limit of condenser temperature application range.
Density and viscosity	Related to pumping rates.
Chemical and thermal stability in contact with materials of construction	Determines rates of decomposition.
Latent heat of vaporization and enthalpy	Related to refrigeration flow rate.
Flammability and toxicity	Safety considerations.
Vapor pressure and specific volume	Affects compressor design.
Chemical reactivity with oil	Must not react to degrade the refrigerant or the oil in an hermetic system.
Miscibility with oil	Must carry oil to moving parts in an hermetic system, especially from low side back to the compressor.
Compatibility with wire insulation, elastomers and plastics	Should not swell, dissolve, or extract from these materials in an hermetic system.
Velocity of sound in vapor	Limits pumping rates.
Solubility of water in refrigerant	Some solubility is desirable so that ice will not restrict metering devices.

Other Factors

Electrical properties	Must not short-out electrical motor windings in an hermetic system.
Leak detection	Leaks should be readily detectable.
Cost	The costs of the refrigerant, the system components, and system maintainance are prime considerations.
Energy requirements	"The saving of energy is as important as the saving of dollars."[10] The energy needed to manufacture and operate the system is becoming increasingly important.
Environmental acceptability	Efforts are being made to reduce the use of the materials which may pose a threat to the ozone layer.

These considerations have been compiled from the ASHRAE Handbook and from direct communications with industry.[8,9]

B. Alternatives to the Chlorofluorocarbons Under Study

There are two broad category alternatives to the use of the subject chlorofluorocarbons in refrigeration systems: (a) utilization of other chemical refrigerants in the mechanical vapor-compression type systems; and (b) utilization of refrigeration systems other than mechanical vapor compression. (A third choice, which is not herein considered, is elimination of refrigeration and air conditioning.)

1. Chemical alternatives for the selected chlorofluorocarbons as mechanical vapor compression working fluids: The ASHRAE Guide and Data Book lists 78 materials which have been used or considered as working fluids in refrigeration systems. Each of these 78 materials has been given consideration as an alternative to fluorocarbons R-11, R-12, R-13, R-113, and R-114. It is beyond the scope of this program to provide a detailed technical analysis of all the refrigerants. MRI has gone through the list of refrigerants and recorded the readily apparent negative aspects of the given materials (Table III-3).

Materials from the ASHRAE which have not thus far been disqualified as viable alternatives as refrigerants, and 12 other compounds having boiling points in the general range of the materials under study, are presented in Table III-4.

TABLE III-3

ASHRAE REFRIGERANTS
(ASHRAE Standard 34-67, ANSI B79.1)

Refrigerant No.	Chemical Name	Chemical Formula	Negative Considerations
Halocarbons			
10	Carbontetrachloride	CCl_4	Stable;[a] possibly reactive with ozone; toxic
11	Trichlorofluoromethane	CCl_3F	Stable;[a] possibly reactive with ozone
12	Dichlorodifluoromethane	CCl_2F_2	Stable;[a] possibly reactive with ozone
13	Chlorotrifluoromethane	$CClF_3$	Stable;[a] possibly reactive with ozone
13B1	Bromotrifluoromethane	$CBrF_3$	Stable;[a] possibly reactive with ozone
14	Carbontetrafluoride	CF_4	Low critical temperature; can use in only very low temperatures
20	Chloroform	$CHCl_3$	Some toxicity; dissolves some insulation
21	Dichlorofluoromethane	$CHCl_2F$	Swells or disintegrates some plastics; high compressor temperature; some toxicity
22	Chlorodifluoromethane	$CHClF_2$	High speed in centrifugals, permeates some elastomers; oil miscibility problems at low temperatures with most oils; high compressor temperature
23	Trifluoromethane	CHF_3	Low critical temperature
30	Methylene Chloride	CH_2Cl_2	Swells or disintegrates some plastics; large compressor displacement; high compressor temperature; some toxicity
31	Chlorofluoromethane	CH_2ClF	Flammable; low critical temperature (can be used as azeotrope)
32	Methylene Fluoride	CH_2F_2	Flammable; low critical temperature
40	Methyl Chloride	CH_3Cl	Flammable, cannot be used with aluminum or magnesium; high compressor temperature; toxic
41	Methyl Fluoride	CH_3F	Flammable

TABLE III-3 (Continued)

Refrigerant No.	Chemical Name	Chemical Formula	Negative Considerations
50*	Methane	CH_4	Flammable
111	Pentachlorofluoroethane	CCl_3CCl_2F	Stable; possibly reactive with ozone
112	Tetrachlorodifluoroethane	CCl_2FCCl_2F	Stable; possibly reactive with ozone; may produce cardiac effects[b]
112a	Tetrachlorodifluoroethane	CCl_3CClF_2	Stable; possible reactive with ozone
113	Trichlorotrifluoroethane	CCl_2FCClF_2	Stable; possibly reactive with ozone
113a	Trichlorotrifluoroethane	CCl_3CF_3	Stable; possibly reactive with ozone
114	Dichlorotetrafluoroethane	$CClF_2CClF_2$	Stable; possibly reactive with ozone
114a	Dichlorotetrafluoroethane	CCl_2FCF_3	Stable; possibly reactive with ozone
114B2	Dibromotetrafluoroethane	$CBrF_2CBrF_2$	Stable; possibly reactive with ozone
115	Chloropentafluoroethane	$CClF_2CF_3$	Stable; possibly reactive with ozone
116	Hexafluoroethane	CF_3CF_3	Low critical temperature
120	Pentachloroethane	$CHCl_2CCl_3$	Toxicity not determined; high boiling point
123	Dichlorotrifluoroethane	$CHCl_2CF_3$	Toxicity not determined
124	Chlorotetrafluoroethane	$CHClFCF_3$	Toxicity not determined
124a	Chlorotetrafluoroethane	CHF_2CClF_2	Toxicity not determined
125	Pentafluoroethane	CHF_2CF_3	Toxicity not determined
133a	Chlorotrifluoroethane	CH_2ClCF_3	Toxicity not determined
140a	Trichloroethane	CH_3CCl_3	Limited flammability
142b	Chlorodifluoroethane	CH_3CClF_2	Limited flammability
143a	Trifluoroethane	CH_3CF_3	Limited flammability
150a	Dichloroethane	CH_3CHCl_2	Flammable

TABLE III-3 (Continued)

Refrigerant No.	Chemical Name	Chemical Formula	Negative Considerations
152a	Difluoroethane	CH_3CHF_2	Flammable
160	Ethyl Chloride	CH_3CH_2Cl	Flammable
170*	Ethane	CH_3CH_3	Flammable
218	Octafluoropropane	$CF_3CF_2CF_3$	No process information available
290*	Propane	$CH_3CH_2CH_3$	Flammable
Cyclic Organic Compounds			
C316	Dichlorohexafluorocyclobutane	$C_4Cl_2F_6$	-
C317	Chloroheptafluorocyclobutane	C_4ClF_7	-
C318	Octafluorocyclobutane	C_4F_8	Poor oil solubility
Azeotropes	Refrigerants		
500	12/152a (73.8/26.2)	CCl_2F_2/CH_3CHF_2	R-12 portion stable; possibly reactive with ozone
501	22/12 (75/25)	$CHClF_2/CCl_2F_2$	R-12 portion stable; possibly reactive with ozone
502	22/115 (48.9/51.2)	$CHClF_2/CClF_2CF_3$	R-115 portion stable; possibly reactive with ozone
503	23/13 (40.1/59.9)	$CHF_3/CClF_3$	R-13 portion stable; possibly reactive with ozone
504	32/115 (48.2/51.8)	$CH_2F_2/CClF_2CF_3$	R-115 portion stable; possibly reactive with ozone
Hydrocarbons			
50	Methane	CH_4	Flammable
170	Ethane	CH_3CH_3	Flammable
290	Propane	$CH_3CH_2CH_3$	Flammable
600	Butane	$CH_3CH_2CH_2CH_3$	Flammable
600a	Isobutane (2-methylpropane)	$CH(CH_3)_3$	Flammable
1150	Ethylene	$CH_2=CH_2$	Flammable
1270	Propylene	$CH_3CH=CH_2$	Flammable

TABLE III-3 (Continued)

Refrigerant No.	Chemical Name	Chemical Formula	Negative Considerations
Oxygen Compounds[c]			
610	Ethyl Ether	$C_2H_5OC_2H_5$	Flammable
611	Methyl Formate	$HCOOCH_3$	Flammable; toxic
Nitrogen Compounds[c]			
630	Methylamine	CH_3NH_2	Flammable; high compressor displacement
631	Ethylamine	$C_2H_5NH_2$	Flammable; high compressor displacement
Inorganic Compounds			
702	Hydrogen	H_2	Flammable; low critical temperature
704	Helium	He	Low critical temperature
717	Ammonia	NH_3	Flammable; toxic; cannot use copper in system
718	Water	H_2O	High boiling point
720	Neon	Ne	Low critical temperature
728	Nitrogen	N_2	Low critical temperature
729	Air	$0.21\ O_2$; $0.78\ N_2$; 0.01 A	Low critical temperature
732	Oxygen	O_2	Supports combustion
740	Argon	A	High operating pressures
744	Carbon Dioxide	CO_2	High operating pressures
744a	Nitrous Oxide	N_2O	High operating pressures
764	Sulfur Dioxide	SO_2	Toxic; high compressor temperature; dissolves insulation
Unsaturated Organic Compounds[c]			
1112a	Dichlorodifluoroethylene	$CCl_2{=}CF_2$	May be toxic
1113	Chlorotrifluoroethylene	$CClF{=}CF_2$	May be toxic, flammable
1114	Tetrafluoroethylene	$CF_2{=}CF_2$	Polymerizes, flammable

TABLE III-3 (Concluded)

Refrigerant No.	Chemical Name	Chemical Formula	Negative Considerations
1120	Trichloroethylene	$CHCl=CCl_2$	Toxic; high compressor displacement; dissolves some insulations
1130	Dichloroethylene	$CHCl=CHCl$	Flammable; high compressor displacement; toxic
1132a	Vinylidene Fluoride	$CH_2=CF_2$	May be toxic
1140	Vinyl Chloride	$CH_2=CHCl$	Flammable; toxic; polymerizes
1141	Vinyl Fluoride	$CH_2=CHF$	Flammable; toxic; polymerizes
1150	Ethylene	$CH_2=CH_2$	Flammable; toxic; polymerizes
1270	Propylene	$CH_3CH=CH_2$	Flammable; toxic; polymerizes

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a/ "Stable" indicates stable in the lower atmosphere, other materials such as R-14 are likewise "stable" but contain no chlorine.

b/ Cardiac effects may also apply to several other chlorofluorocarbons in high concentration under conditions of stress. This effect is not restricted to F-112.

c/ These compounds are generally far more reactive than the materials under study, and in general, would not be expected to possess the required chemical stability.

Note: * These materials appear in the halocarbon section but they are not halocarbons.

TABLE III-4

MATERIALS FOR CONSIDERATION AS ALTERNATIVE REFRIGERANTS[a]

Refrigerant No.	Chemical Name	Chemical Formula	Boiling Point °F	Boiling Point °C	Melting Point °F	Melting Point °C
22	Chlorodifluoromethane	$CHClF_2$	-41.4	-40.8	-256	-160
123	Dichlorotrifluoroethane	$CHCl_2CF_3$	79	26	-	-
124	Chlorotetrafluoroethane	$CHClFCF_3$	-	-	-	-
124a	Chlorotetrafluoroethane	CHF_2CClF_2	-	-	-	-
125	Pentafluoroethane	CHF_2CF_3	-	-	-	-
133a	Chlorotrifluoroethane	CH_2ClCF_3	-	-	-	-
142b	Chlorodifluoroethane	CH_3CClF_2	14.5	-9.7	-	-
218	Octafluoropropane	$CF_3CF_2CF_3$	-38	-39	-	-
C316	Dichlorohexafluorocyclobutane	$C_4Cl_2F_6$	-	-	-	-
C317	Chloroheptafluorocyclobutane	C_4ClF_7	-	-	-	-
C318	Octafluorocyclobutane	C_4F_8	21.5	-6.0	-42.5	-41.4
1112a	Dichlorodifluoroethylene	$CCl_2{=}CF_2$	-	-	-	-
1113	Chlorotrifluoroethylene	$CClF{=}CF_2$	-	-	-	-
1132a	Vinylidine Fluoride	$CH_2{=}CF_2$	-	-	-	-
-	Perfluoropropylene Oxide	$CF_3\overline{CFCF_2O}$	102	39	-175	-283
-	Perfluorobutane	nC_4F_{10}	28	-2.2	-198	128
-	Perfluorotrimethylamine	$(CF_3)_3N$	12.4	10.9	-	-
-	bis(Trifluoromethyl)sulfone	$(CF_3)_2SO_2$	60	15.6	-	-
-	Pentafluoroethyl Sulfur Pentafluoride	$C_2F_5SF_5$	66	19	-	-
-	bis(Trifluoromethyl)sulfur Tetrafluoride	$(CF_3)_2SF_4$	69	20.5	-	-
-	Perfluoroacetone	$(CF_3)_2CO$	-17.5	-27.5	-188	-122
-	Trifluoromethyl Sulfur Pentafluoride	CF_3SF_5	-4	-20	-124	-87
-	Perfluoropropane	C_3F_8	-34.6	-37	-297	-183
-	Perfluorodimethylether	$(CF_3)_2O$	-74.2	-59	-	-
-	Perfluorohexane	$n\text{-}C_6F_{14}$	136	58	< -102	< -75
-	bis(Pentafluorosulfur)-difluoromethane	$CF_2(SF_5)_2$	75.3	59.6	-94	-70
-	Tetrafluoroethane	CHF_2CHF_2	-15	-26	-	-

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[a] Those materials with an assigned refrigerant number were taken from the ASHRAE list of refrigerants; the other materials are, in general, experimental materials.

The 12 compounds are shown for illustrative purposes and do not represent an exhaustive search of the literature. In all probability, some of these materials will be eliminated from consideration for given applications because of inappropriate properties such as boiling point, critical temperature, vapor pressure, specific volume, and toxicity.

Chlorofluorocarbon producers are, at this point, interested in alternatives for chlorofluorocarbons which could be produced in existing facilities now producing R-11 and R-12. R-21 and/or R-22 could be produced in facilities now producing R-11 and R-12 at a conversion cost of approximately 15% of the current replacement cost of those facilities.[11] In addition, a large capital investment for new chloroform capacity will be required. Although there exists some negative considerations to the use of R-22 in some applications, this material is by far the leading candidate as an alternative to R-11 and R-12. Many of the end-product manufacturers are hesitant to design for the use of R-22, however, for fear that R-22 will also come under control. Most of the other materials listed in Table III-3 could not be produced in existing facilities without very significant plant changeover. The technology of high volume production is said to be unavailable for C_3 and C_4 series materials.[9] The cost of chlorofluorocarbons is directly related to the number of F atoms in the molecule, and the production of perfluorinated materials requires very high energy consumption.

It is also possible that blends or mixtures of some of the refrigerants listed in Table III-3 may be formulated that would have better end properties than the individual components. These would not be azeotropic mixtures but physical mixtures. Most refrigeration systems have sufficient mixing action within the system that any leakage on the vapor side would probably not result in any significant fractionation of the refrigerant mixture.[9]

2. Cycles other than mechanical vapor compression: Five systems other than mechanical vapor compression have been considered in this study. They are absorption, thermoelectric, steam jet, liquid nitrogen, and the air cycle. Detailed technical discussions of these systems are provided in the ASHRAE Guide and Data Book. A later generation air cycle system, Rovac, is now in the prototype stage of development. A technical paper describing this system and the claims of the inventor is provided in Appendix B.

a. Absorption cycle:

> "As in the vapor compression cycle, the refrigerant is pressurized, liquified, cooled and then allowed to vaporize in the evaporator where it absorbs heat to accomplish refrigeration. However, instead of using a compressor to pressurize the refrigerant, it is cooled to permit liquefaction at a low pressure by absorption in a miscible absorbent fluid and pumped as a liquid to the generator. Heat is applied at the generator to drive off the refrigerant as a vapor and to pressure it. The refrigerant is then cooled in the condensor to form a pressurized liquid for use in the evaporator again."[1]

Two absorption systems using two different combinations of working fluids have been used, and are in use today. One is a lithium bromide-water cycle; the other is the ammonia-water cycle.[12] The lithium bromide-water system is used in special applications for comfort air conditioning, and cannot be used below the freezing point of water. The ammonia-water system can be used in both air conditioning and refrigeration applications. Some important factors to be considered for these systems are as follows:

1. The technology for manufacturing absorption equipment is well established, but is used by only a limited number of companies.[12]

2. Absorption systems are heavier and more expensive than mechanical vapor compression systems. It is commonly quoted that these systems are less efficient than compression cycle systems. This misconception arises because the COP values of the compression cycle is based on the heat equivalent of the electrical energy fed to the motor and ignores the thermal losses at the power plant producing the electrical energy. When absorption and compression cycles are compared on the same basis, i.e., the Btu of cooling per Btu of fuel energy used, the COP values are very nearly the same.[10] Absorption chillers are used only where waste heat is available.[4] (The heat probably does not have to be "waste," but the economics of the energy source is a prime consideration.)

3. While the absorption equipment is larger than the equivalent sized compression equipment, its selling point has been its lower cost of operation. As the costs of both gas and electrical energy rise, it may be that the lower operating cost of absorption systems will overcome their higher initial costs.[10]

4. Ammonia is toxic to humans, with a threshold limit value (TLV) of 25 parts per million (ppm), as compared with the high TLV of 1,000 ppm for fluorocarbons. It also forms an explosive mixture in air at 16% concentration. Ammonia is not suitable for use in units within buildings where human exposure is possible.[3]

5. Ammonia is very corrosive to brass and bronze, and has a higher tendency to leak than do common chlorofluorocarbons.

6. Absorption units are less efficient in energy consumption than mechanical systems, and (for appliances) could be used only where natural gas can be used as a heat source.[10]

7. An estimated 300,000 absorption refrigerators are sold per year in the U.S. Most of these go into the recreational vehicle or motor home market. An estimated 25,000 absorption units are sold per year for central air conditioning and chillers accounting for approximately 1.25% of the market. Of the 25,000 units, approximately 80% are for residential and small commerical applications.[13]

8. In the chiller market, approximately 2% of the total is absorption units. All of these units are lithium bromide systems, and the cost is approximately twice that of chlorofluorocarbon systems.[7]

9. Operating efficiencies of absorption refrigerators and freezers are considerably below those of vapor-compression units.[1] The use of "waste" heat may be an opportunity to reduce the energy input to the system and reduce overall operating costs plus energy consumption.

10. Ammonia or lithium bromide can be used where steam is available, but absorption systems are inefficient when fired with an oil burner.[14]

11. System should be perfectly level.

b. Thermoelectric system: When electrical energy is forced to flow through a thermocouple junction (two dissimilar metal wires connected at one end), heat is absorbed or rejected at the junction. The important factors to be considered for thermoelectric cooling are as follows:

1. The heating and cooling functions of a thermoelectric system can be interchanged by reversing the polarity of the direct current applied to it.[1]

2. Since there are no moving parts, there is nothing to wear out or to generate noise.[1]

3. It is practical to make a system of very low refrigerating capacity or a system of large capacity if many couples are used.[1]

4. The system will operate in any position.[1]

5. The system is much less efficient than a compression system.[1,15] This low efficiency may be a major factor in considering these systems as alternatives.

6. Most units are in 30 to 200 Btu/hr range[15] (12,000 Btu/hr ≃ 1 ton).

7. System is reliable, safe, quiet, and provides weight and size advantages in given applications.[15] However, a major appliance manufacturer disagrees with the reliability factor and states that these systems lack reliability.[10]

8. While the units are economical to produce in low cooling capacity ranges (~ $10/40 Btu unit), the scale-up cost is linear.[15]

9. Units are presently used as follows:[15]

a. To cool sensitive electronic systems such as sensors in military missiles.

b. In commerical airliners to cool drinking water.

c. In very small refrigerators for recreational vehicles and boats.

d. To cool epoxy for dental applications.

10. The U.S. government has sponsored development of units up to 9-ton capacity for use on submarines.

11. A Swedish firm is contemplating production of a 1,000 Btu/hr room air-conditioner using thermoelectric units (the smallest U.S. produced room air-conditioner is ~ 4,000 Btu/hr).15/

12. There are some practical problems in thermoelectric systems with regard to the dissipation of heat and the practical application of the cooling effect.

13. Larger units could be practical where very large amounts of DC power is readily available.

c. Steam jet: The steam-jet refrigeration cycle is quite similar to more conventional refrigeration cycles with an evaporator, a compression device, a condenser, and a refrigerant as the basic system components. Instead of a mechanical compression device, the system characteristically employs a steam ejector or booster to compress the refrigerant to the condenser pressure level.

Water is used as the refrigerant, and the cooling effect is produced in the steam-jet refrigeration cycle by the continuous vaporization of a part of the water in the evaporator at a low absolute pressure level.1/

Considerations are as follows:

1. The system is now used for applications such as freeze-drying of foods, chemical crystallizers, etc.1/

2. The largest users are paper pulp operations in which ClO_2 water is chilled to ~ 40°F for bleaching. Some units are used for hospital operations.16/

3. The units are initially less expensive, less troublesome, and essentially maintenance-free. An operating engineer does not have to be on duty.1,16/

4. The system is simple, rugged, vibration free, highly reliable and low in cost.[1]

5. While a given manufacturer sells 5 to 20 units/year in the 100 to 3,000 ton range, the system is technically feasible down to ~ 1-ton capacity.[16]

6. Large quantities of water are needed for the larger units and utility costs are likely higher.[16] (Obviously, high-pressure steam must be available.) The requirements of a high pressure steam source and large quantities of water should seriously limit its general consideration as an alternative.[10]

7. The system tends to be noisier than conventional systems.[16]

8. The lower the application temperature, the less the system is competitive with chlorofluorocarbon systems.[16]

d. Liquid nitrogen: Liquid nitrogen (LN_2) is used as a refrigerant for refrigerated trucks and trailers where a hard freeze is required (and for cryogenic applications).[1]

Other important factors are as follows:

1. The major disadvantages of LN_2 are constant replenishment and the special care required in handling and distribution because of its very low temperature.[1]

2. LN_2 refrigeration is technically feasible to adapt to any required temperature range, but it is not economical. No one uses LN_2 at use temperatures greater than -40°F.[17]

3. Systems are not produced in large numbers. At present a closed system the size of a home refrigerator or air conditioner and operating at ~ 20°K (-253°C or -423°F) would cost ~ $15,000.[17]

4. LN_2 production requires a great amount of energy--the efficiency ratio (energy output to energy input may be 1:100).[17]

e. Air-cycle: Refrigeration in a simple open air-cycle system is obtained by three basic steps: (1) compression; (2) heat transfer; and (3) expansion accompained by work extraction. Air-cycle refrigeration systems are more commonly used in the air-conditioning of aircraft than in surface and stationary applications, because the lightweight compact equipment typical of air-cycle systems usually offsets its inherently low efficiency. The development in recent years of lightweight vapor-cycle refrigeration, with high speed compressors, has resulted in a decrease in the use of air-cycle equipment in aircraft systems. Air-cycle air conditioning has not been found to be economical in residential and commercial buildings because of the high power required. However, it is used in other specialized applications where efficiency and operating costs are not the primary factor. For example, air-cycle cooling units are used with portable gas turbine power plants to provide environmental control for remotely located, temporary, military bases. Air-cycle refrigeration may be designed and operated either as an open or a closed system. Open air-cycle systems have been widely used both in military and commerical airplanes since the end of World War II.[1]

The major problem for the standard air-cycle systems is the inherent low efficiences.[1]

f. Rovac air-cycle: The Rovac system is now in the prototype stage of development, and uses air as the refrigerant. The system is described by its developer* as a "multifluid mixed phase cycle which is a hybrid of the reverse Brayton cycle (air-cycle) and the reverse Rankine cycle (chlorofluorocarbon)."[18]

A large portion of the development work on the system was accomplished on contracts to the U.S. Air Force for production of prototype air conditioning units for aircraft.[18] The system is said to be technically feasible for a wide range of end-use applications: automobile air conditioners; transport refrigeration; refrigerators; freezers; supermarket applications; residential air conditioners and heat pumps;[19] and possibly commercial chillers.[18] A prototype window air conditioner has been produced for the U.S. Army. Rovac's in-house efforts have been concentrated primarily on the development of an air conditioning system for automobiles. Prototype units have been or are being evaluated by Chrysler Corporation[20] and by General Motors Corporation,[21] and information on the system was solicited from these companies. Rovac also has working arrangements with a number of foreign automotive manufacturers.[18]

Other applications for which Rovac is now designing prototypes include residential heat pumps and units for transport refrigeration. While major manufacturers of air conditioning and refrigeration systems are understandably reluctant to speculate on a system which is still under development, most of these companies have likely given the system preliminary consideration.

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* A technical paper authored by the inventor and patent holder is attached to this report as Appendix B. The paper gives a technical description of the system and records the claims of the developer. The data in the paper are said to be approximately 2-years old, as of this writing, and many technological improvements are said to have been made in the past 2 years. The system is further described in the November 1975 issue of Air Conditioning and Refrigeration Business.

Technical data now available are primarily from one source, Rovac; and those data are for the automobile air conditioning prototypes. Some back-up information has been obtained from the U.S. Air Force. Rovac claims that the automobile system could be marketed in its present stage of development, but admits that there are areas in which improvement is needed:

1. While the system is now competitive from an efficiency standpoint, computer programs indicate that substantially better efficiencies can be obtained.

2. The vane material must have extremely good dimensional stability (thermal coefficient of expansion < 6 μin/in/°F) over the operating temperature range, and, while the carbon vanes are now being used meet this criterion, there is a problem with carbon "overfilms" (carbon dust combines with grease to form a sludge).

3. Long-term reliability must be performed (the longest continuous operation of 300 hr provided satisfactory performance).[18]

Rovac claims for the automotive system can be summarized as follows:

1. The cool-down rate is extremely fast as compared to conventional systems.

2. The weight of the total system is approximately 40 lb as compared to approximately 12t lb for a conventional system.

3. The cost should be approximately two-thirds that of a conventional system.

4. Energy savings, in terms of gasoline usage, should be approximately one-third.

5. The temperatures achieved in operation are said to kill bacteria and some spores, and the system removes pollen and smoke from the air.

6. The unit is capable of operating on either recirculating or fresh-air modes.

7. The unit operates satisfactorily at all engine speeds, although the cooling capacity is a function of the engine speed.

8. The system is satisfactorily quiet, although improvements are still being made.

9. The system can be designed for cooling to -50°F.

The project officer for the Air Force contracts[19/] substantiates Rovac's claims, and adds the following comments:

1. Rovac is probably being conservative in claiming energy savings of one-third.

2. The system is easily maintained and repaired, and essentially no special training is needed for a good mechanic.

3. No great retooling cost is anticipated. The system has fewer parts than conventional systems, and standard metal-working machines are used for production.

4. The old air-cycle turbine used on aircraft operated at 60,000 to 80,000 rpm, and the Rovac prototype operates at less than 4,000 rpm.

5. High-compression ratio machines should be able to achieve a temperature of -100°F.

6. The Rovac system will be flight tested within the next 3 years. The Air Force also expects to use the Rovac system in ground-level air conditioning applications.

7. The cost of the aircraft units is much higher than that of an automobile system because of higher capacities and closer tolerances. Present aircraft systems cost $9,000 to $10,000, and the Rovac aircraft system is projected to cost $3,500.

MRI personnel have not seen any Rovac system in operation or performed any testing on the system. Dr. Thomas Edwards of the Rovac Corporation visted MRI, and made a slide and film presentation to a group of scientists and engineers. The overall consensus of this group was that the concept appears viable from mechanical and thermodynamic standpoints, based on available information. Fabrication of component parts appears to be within the present state of the art for mass-produced items; however, final materials-selections may require development of special fabrication techniques. Concern was expressed in the following areas:

1. Machine size and compression ratios do not appear to have been optimized.

2. Inasmuch as the efficiency of the system is dependent partly on the humidity of the intake air, questions still need to be answered on operation in low-humidity conditions.

3. Filtering of high-solids-loading intake air may present a problem in terms of restricted air flow and clogging or damaging internal components.

4. There is some concern with the choice of the vane material and the inherent losses because of the vanes cycling through the relatively extreme temperature differential in the circulator.

5. Longer-term reliability tests should be made using in-service conditions.

6. A situation might arise wherein engine combustion products could be aspirated into the passenger compartment through a leak in the inlet air duct.

The question was asked of Rovac: "Why are you not now in production?" The following statements have been excerpted and pharaphrased from Rovac's lengthy written response:

> ". . . Rovac is a very small company developing a rather large technology. Due to the size of the technological development relative to the size of the company resources, the level of development needed for the generation of adequate warranty data has not been reached. Rovac is increasing the performance of the machine with each passing month and is still in a learning process in methods of manufacture. Another consideration is the matter of design and procurement of production equipment.
>
> "In the event Rovac was fully satisfied with the state of development of the system, it would take 12 to 18 months to have the first machines off a production line. In the event that a large company joins Rovac in the final development of the technology, a much higher degree of productivity could take place on a shortened time frame. However, there would still be the minimum 1-year situation. Further, the pragmatics of U.S. automakers are such that the technology would not be integrated on a wide scale into that industry for approximately 2-1/2 to 3 years.
>
> "In summary, Rovac is not in production because it wants to fully prove the product and gain all warranty data for its financial planning and to ensure that it launches into the marketplace with a fully acceptable product. . ."

C. Applicability of Alternatives in Specific Use Areas

In addition to the previously discussed attempts to determine technically feasible alternative systems, manufacturers of a wide range of end-use products, as well as the respective trade associations, were contacted. They were asked what they considered technically feasible chemical or mechanical alternatives to the use of the selected chlorofluorocarbons. Early in the program, efforts were also made to determine the overall economic impacts and resulting net changes in U.S. employment.

The efforts to determine the economic impacts of converting to alternatives for the selected chlorofluorocarbons in air conditioning and refrigeration applications were not successful. The reasons for this are severalfold:

1. In contrast to the aerosol industry, the air conditioning and refrigeration industry has had, until the ozone question arose, no economic driving force to convert from the chlorofluorocarbons. The overall trend has, in fact, been away from the use of the nonchlorofluorocarbon alternatives because of flammability, toxicity, cost, and energy-consumption considerations.

2. The most often mentioned alternative to the materials in question is R-22; however, a refrigerant is chosen for a given end use because of combination of previously described considerations, and, while R-22 could undoubtedly be utilized in many applications currently using the materials in question, substantial redesign and retooling would be required. Most manufacturers are concerned that R-22 will be added to the list of chlorofluorocarbons which may come under regulatory action, and therefore, have not finalized the design work which would necessarily precede estimates on costs of conversion.

3. The industry is now greatly concerned with energy conservation, and any systems conversions will need to be analyzed in terms of energy consumption. These analyses are not generally available.

4. Individual appliance manufacturers and the Association of Home Appliance Manufacturers are hesitant to reveal present costs and market shares and there is conflicting information on projected sales figures. Efforts to project accurate sales figures are hampered by the present state of the overall economy and by the already demonstrated effect of possible regulatory controls on chlorofluorocarbons. (Chemical Week's projected market for chlorofluorocarbons has dropped substantially since mid-year because of the ozone question.)

The detailed economic data and product growth rates are so incomplete as to render its incorporation into this report to be premature. Some detailed information is available in the open literature.[22-29] Gross economic considerations of converting to alternative systems are provided where applicable. Most appliance manufacturers believe that there would be a negligible net change in their employment figures because of conversions.[10,30] Table III-5 summarizes the applicability of alternatives to given end uses.

TABLE III-5

APPLICABILITY OF ALTERNATIVES TO END-USE PRODUCTS

			Alternate Systems				
			Absorption				
Type of Equipment	Fluorocarbon Refrigerants Now Used	Candidate Vapor Compression Refrigerants[a]	Lithium Bromide	Ammonia	Thermoelectric	Steam Jet	Air Cycle (Rovac)
Appliances							
Refrigerators and Freezers	R-12	R-22,R-502, and others	No	Yes, but toxic	Yes, but inefficient	No	Not at present
Water Coolers	R-12	R-22,R-502, and others	Yes	Yes, but toxic	Yes, but inefficient	No	Not at present
Ice Makers	R-12	R-22,R-502, and others	No	Yes, but toxic	Yes, but inefficient	No	Not at present
Dehumidifiers	R-12	R-22,R-502, and others	Yes	Yes, but toxic	Yes, but inefficient	No	Not at present
Mobile Air Conditioning	R-12	R-22,R-502, and others	Yes no design	Yes, but toxic	Yes, but inefficient	No	Possibly in future (under development)
Centrifugal Chillers	R-11,R-12,R-22,R-500,R-114	R-22,R-502, and others	Yes	Yes, but toxic	Yes, but inefficient	Limited	Not at present
Reciprocating Chillers	R-11,R-12,R-22	R-22,R-502, and others	Yes	Yes, but toxic	Yes, but inefficient	Limited	Not at present
Mobile Refrigeration	R-12,R-502	R-22,R-502, and others	No	Yes, but toxic	Yes, but inefficient	No	Possibly in future (under development)
Commerical Refrigeration	R-12,R-502,R-22	R-22,R-502, and others	No	Yes, but toxic	Yes, but inefficient	Limited	Not at present

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[a] See list provided in Table III-4, p. III-15.

1. Appliances: Although R-12 was once used in room air conditioners, all U.S. made room air conditioners, commerical unitary coolers, and residential central air conditioning systems (excluding absorption units) now use R-22.[10] Accordingly, these appliances will not be further considered. Appliances now using R-12 (or R-502 in some commerical applications) include refrigerators, freezers, dehumidifiers, ice makers, etc. Efforts in this area were concentrated on refrigerators and freezers which, for the category of appliances, represent the largest usage of the specified materials.

a. Absorption system: The ammonia-water absorption system was once used in household appliances, and is a technically feasible alternative to the R-12 system. This system is currently used in home appliances in some European countries[10] but "most" U.S. made absorption refrigeration systems go to the recreational vehicle or motor-home market.[13] Absorption systems are heavier and more expensive than mechanical systems[4] and are said to be competitive only where natural gas is available as a heat source[10] or where "waste" heat may provide an opportunity to be used in conjunction with other energy sources. Other considerations such as toxicity and flammability have been previously discussed. No other usable refrigerants have been identified for the absorption system.

b. Thermoelectric: Thermoelectric cooling units are technically feasible for appliances, and very small refrigerators are now produced for recreational vehicles and boats. The thermoelectric system is inefficient in power consumption, and has some practical problems in the dissipation of heat and application of the cooling effects. In all probability, it is not competitive in typical appliance applications because of cost considerations.[8,10]

c. Steam jet: The steam-jet system is technically feasible at minimum capacities down to 1 ton.[16] Steam is not generally available for appliance uses, and the system is not cost-competitive with mechanical vapor-compression systems at low temperatures.

d. Liquid nitrogen: The use of LN_2 for appliances is technically feasible.[8,17] The system would not be cost-competitive, and energy consumption would be prohibitive.[17]

e. Air cycle: The conventional air cycle would not be adaptable to appliance usage because of size, noise, poor efficiency, etc. The greatest drawback is the lack of efficiency.[10]

f. Rovac: No prototype unit has been produced for the subject applications, but the system may be technically feasible for such applications.[18] The system thermodynamics were reviewed approximately 1 year ago by a major appliance manufacturer and, at that time, did not appear to be efficiency-competitive.[10] The industry will continue to follow the development of this system.

g. Alternative vapor compression refrigerants: Appliance manufacturers are not seriously considering the previously used refrigerants such as sulfur dioxide, methyl chloride, and hydrocarbons because of toxicity and/or flammability considerations or carbon dioxide because of high pressures and poor efficiencies.

R-22 is probably the leading candidate alternative refrigerant for appliance applications.[19,31] R-22 was the second choice of a large compressor manufacturer which preferred R-502.[8] General technology is available for both of these materials inasmuch as they are now being used in some applications. However, R-502 is an azeotropic mixture of R-22 (48.8%) and R-115 (51.2%); the R-115 component of R-502 is perhalogenated and may come under regulatory control. R-22 is also more economical to produce than is R-502. Besides the advantage of available technology, R-22 could be produced in existing facilities with relatively small capital investment (~ 15% of current replacement costs)[11] plus the additional costs for the new chloroform capacity. In conversion from R-12 to R-22, the carbon tetrachloride producers would be hard-hit, since R-12 is made from carbon tetrachloride and R-22 is made from chloroform.

Although R-22 is a technically feasible alternative to R-12 for use in most appliances, several problem areas have been delineated in designing for that conversion. R-22 systems operate at higher pressures and higher compressor temperatures than do R-12 systems. The reliability and life of a product are said to be inversely proportional to the compressor's operating temperature.[8] It has been stated, for R-22 systems, oil stability is a problem,[4] and that R-22 stability is a problem.[32] One large manufacturer and other industry sources believes neither of these problems to be a serious concern.[9,10] It is quite often stated that there is a miscibility problem with R-22 and the refrigeration oil at low temperatures.[7,8] A chlorofluorocarbon producer[9] states that an oil is now available that is completely miscible with R-22 in all proportions at temperatures as low as -115°F.

One refrigerator manufacturer[31] has previously produced prototype refrigerators operating on R-22. Data on field testing and accelerated load testing were not available. There may be a problem with compressor valve mechanisms operating at the high pressures of an R-22 compressor (the compression ratio in a refrigerator may be approximately 10:1 as compared to approximately 5:1 for a room air conditioner).[31]

Large costs of retooling would result from the conversion from R-12 to R-22 units.[8,10,31] One compressor manufacturer[8] estimated the retooling costs for a 300 compressor per hour line to be $10 to $12 million (it presently operates a total of five lines). Another appliance manufacturer estimated its retooling costs to be approximately $50 million.[10]

Prototype R-22 units would have to undergo field testing, energy consumption testing, and standard Underwriters Laboratory tests before they could be marketed.

2. Industrial air conditioners and chillers: Very little information has been obtained on alternatives for this end-use category. A general discussion of the problems involved appear in Reference 12.

a. Absorption: Absorption systems are technically feasible for these applications within the limitations addressed in Section C (1) "Appliances." Absorption systems are used where steam is available for energy input[14] or other "waste" energy is available.[4] Ammonia can be used in reciprocating compressors where the previously discussed limitations can be tolerated.

b. Steam jet: The steam jet is a technically feasible alternative to those applications using R-11, R-12, and R-13 where steam and water are available in quantity, and where size limitations are not important.

c. Alternative vapor compression refrigerants: While R-13, R-114, and R-22 are used in some applications, the chiller market is generally broken down as two-thirds R-11 and one-third R-12 and R-500.[7] No technology is available for mechanical vapor compression refrigerants other than the above.[7] Therefore, R-22 would appear to be the most viable alternative to the materials in question. The problem of converting to R-22 is discussed in Reference 12.

Some large chiller manufacturers would not discuss the problem on the telephone (time and cost considerations precluded personal conferences) or asked not to be quoted on the small amount of information offered.

The only other alternative mentioned as being technically feasible was to use multiple R-22 reciprocating compressor units, currently limited to approximately 100 tons maximum cooling capacity, to attain the cooling capacity now obtained from centrifugal units using R-11 (100 to 1,500 tons) and R-12 (1,000 to 6,000 tons). R-22 is now used in centrifugal units greater than 5,000-ton capacity. (The source offering this alternative asked not to be quoted.) The usage ranges for the various systems were provided by Reference 4.

3. Automotive air conditioning: R-12 from mobile air conditioning is estimated to account for 33.3% of the total chlorofluorocarbon refrigerants being emitted to the atmosphere.[2] Accordingly, a proportionately large amount of this program's effort was directed at identifying alternative refrigerants or systems for this end use. Presently, approximately 7 million automobiles (including light trucks) are being air conditioned each year. Of this number approximately 1/2 million units are add-ons.[5]

Alternatives to the nonhermetic R-12 systems now being used which have been considered include: R-22 systems; alternative vapor compression sytems; other vapor compression refrigerants; absorption systems; hermetically sealed R-12 systems; and the air-cycle systems.[20] The American Society of Heating and Refrigeration and Air Conditioning Engineers (ASHRAE) is currently preparing a report on alternative refrigeration systems, time frames needed for change, and affected industries.[33] The pertinent information will be presented at a seminar in June 1976 at the ASHRAE Annual Meeting, Seattle, Washington.[8]

a. R-22 systems: R-22 systems have been, and are now being, strongly considered as an alternative to the R-12 system, and would likely be the most readily adaptable alternative system.[34-36] Chrysler Corporation marketed automobiles equipped with an R-22 system in 1952 and 1953.[20] This system contained all copper fittings, and did not incorporate a clutch. The mechanism was mechanically engaged in the spring and disengaged in the fall; therefore, the unit ran throughout the summer months with a constant load on the automobile engine. This type of operation would very probably be unacceptable in the modern market. More recently, prototype R-22 units have been built by the after-market (add-on) industry.[36] The pragmatics of the after-market industry differ from those of factory installers, and R-22 add-on units could likely be marketed in a much shorter time from the date of a decision to control R-12.

Development of a nonhermetic R-22 system for automotive use would require a number of considerations which are delineated, not necessarily in order of importance, as follows:

1. R-22 systems operate at higher pressures than do R-12 systems; leakage through flexible rubber hosing is a problem.[7,20,35,36] Water-vapor permeability of the hosing is also a concern.[35] These problems can be minimized by proper design.

2. The compressor would have to be redesigned to accomodate the increased pressure and vibration.[20]

3. The condenser would have to be enlarged, or auxiliary blowers would have to be used.[36]

4. Controls would have to be redesigned.[20]

5. Manufacturers are concerned that R-22 may be controlled.[34]

6. Very small cars which could use R-12 systems may not have the power to operate a R-22 system.[36]

7. The time-frame for conversion by auto makers is estimated at 3[20] to 5[34] years from the time of decision. Most of this time would be needed for retooling.[20]

8. The increased cost of an after-market (add-on) R-22 system would be approximately 7 to 10%.[36] No cost figures are available on factory-installed units.

9. R-22 does not have the worldwide availability of R-12.[35]

b. Alternative vapor compression systems: The mechanical vapor compression system using ammonia has been discounted because of the toxicity of that refrigerant. This would be especially hazardous in the aftermath of an automobile collision.[20]

c. Other vapor compression refrigerants: The automotive industry has no information on new refrigerants which might be forthcoming from refrigerant producers.[20,34] No technology is available for alternative refrigerants other than R-22.[7] Application of a new refrigerant may take 7 to 9 years.[34] Hydrocarbons and other systems have been considered, but the information is being retained for incorporation in the forthcoming seminar at the ASHRAE Annual Meeting in Seattle, Washington, in June 1976.

d. Absorption system: Absorption systems have been considered for automotive use.[20,33] The ammonia system has been discounted because of its toxicity.[20] The lithium-bromide system could be applied, but approximately one-half of the heat-energy required would have to come from a source other than that available from the automobile engine, and the condenser would have to be approximately double the size of the present condenser.[20] Ford Motor Company is said to have presented a paper dealing with automotive lithium bromide absorption systems to the Society of Automotive Engineers. A copy of that paper has not been received as of this writing. Work is also in progress on absorption systems other than ammonia and lithium bromide,[20] but we do not know who is performing the work.

e. Hermetically sealed vapor compression system: Hermetically sealed units using either R-12 or R-22 are said to be technically feasible for automotive air conditioning at an increased wholesale cost of approximately $150. The unit would operate on a 12-V system, and no hoses would be necessary.[8] A 5 hp hermetically sealed DC motor would be required and would be difficult to package.[20]

f. Air-cycle system: The Rovac air-cycle system has been or is being considered by Chrysler Corporation, General Motors Corporation, and several foreign automobile manufacturers.[18] Rovac is now working on the installation of a Rovac air conditioning system in a General Motors automobile,[21] and technical data are not yet available from that source.

Chrysler Corporation[20/] has performed initial testing on a Rovac air conditioning system installed in an automobile by Rovac. While Chyrsler believes the system may find extended use in the future, there were certain reservations about the system in its stage of development at the time of the testing. The following comments were offered for consideration:

1. Manufacturability at a reasonable cost on a mass production scale has not been demonstrated.

2. The efficiency is linear with speed in a rotary system, but not in a piston compressor. The basic problem is to obtain sufficient volume displacement in the compressor.

3. The efficiency of a rotary compressor is inherently more sensitive to leakage than is a piston compressor.

4. There was concern because of the close tolerances demanded as well as possible thermal distortion of components.

5. The alignment of the circulator end plates is very critical.

6. The coefficient of performance (COP) of the test unit was not substantially different from the average conventional unit.

After all problems are solved at Rovac, it is estimated that 3 years would be needed to test the system completely, and an additional 3 years would be needed to design and tool for manufacture.

4. Other end-uses: The same considerations provided for appliances, industrial air conditioners and chillers, and automotive air conditioners can generally be applied to other end uses such as food store applications, automatic merchandising equipment, and transport refrigeration. One basic difference is the claim by Rovac that a transport refrigeration system, now being designed, will take advantage of moisture-laden output air for maintaining very high humidity conditions in applications such as produce transportation.

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IV. AEROSOL INDUSTRY

Aerosol products were first introduced on the consumer market in 1947, following the successful development of reliable pressurizing and delivery systems during World War II. The war-time aerosol insecticide "bomb" used the volatile chlorofluorocarbon liquid, Freon® 12, as the propellant.[1] This development, supported by the adoption of additional propellants and improved valve and atomizer designs, spurred the growth of what is today a $3 billion industry.[2] Hundreds of personal, household, and commercial products are now available in aerosol form, and although many propellant systems are employed, the chloroflurocarbons are the most widely used and are currently the cause of much environmental alarm.

The results of our study of possible chemical and mechanical alternatives to the use of those chlorofluorocarbon aerosol propellants of concern are presented in the following order: a brief description of the nature of the aerosol industry today; an introduction to the kinds of aerosol technologies and to the specific propellant chemicals that are in use; surveys of the requirements that a successful alternative must meet, and of the candidate propellants or mechanical devices; a discussion of potential alternatives for specific aerosol uses; and finally, an analysis of production data for potential alternatives for the subject chlorofluorocarbons.

A. Development of the Aerosol Industry, Aerosol Systems and Propellants

This section presents a brief history of the industry's development, discusses the basic aerosol systems, and identifies the commonly used propellants.

1. Development of the aerosol industry: Early research on aerosol technology produced patents as early as 1862. Notable patents were issued on a perfume atomizer pressurized with carbon dioxide in 1903, on a dimethyl ether propellant system in 1931, on fluorinated hydrocarbons propellants in 1933, and on propellant blends of hydrocarbons, methyl chloride, and dimethyl ether in 1938.[1]

The first commercial fluorocarbon,* Freon® 12, was developed by General Motors in 1928 and commercialized by E. I. du Pont de Nemours and Company in 1930[3] as a refrigerant fluid. Freon® 12 (CF_2Cl_2) was also a model propellant, possessing both ideal vapor pressure and boiling point. During World War II, the first portable aerosol dispenser was developed and F-12 was used as the propellant.[1]

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* The term fluorocarbon has been widely used to refer to chlorofluorocarbons.

Aerosol products were not available to the consumer until 1947. Production in that year was 4.3 million units, almost exclusively insecticides. The development of additional fluorocarbon propellants (e.g., F-11 and F-114) made possible, through blends, the formulation of propellant mixtures having a wide range of vapor pressures and boiling points. These propellant blends are nontoxic, nonflammable, and compatible with a range of products. Because of these qualities, the aerosol product market grew tremendously between 1947 and 1974. By 1974, United States sales of aerosol products reached almost 3 billion units and now includes a variety of products. The chlorofluorocarbon propellants are used in approximately 50% of the aerosol units, hydrocarbon propellants are used in 45% of the units, and nitrous oxide and carbon dioxide are used in the remaining 5% of the aerosol units.[4/]

Market surveys showed that in 1971, the average number of aerosol units (including food products) per household reached 40.8. Approximately one-half of these units were personal products and about one-fourth were household cleaners, laundry products, etc.[5/] Thus, in less than 30 years, the aerosol products have become a major consumer market.

2. Basic aerosol systems: Aerosol propellants are of two basic types: liquefied gases and compressed gases. The liquefied gases usually have boiling points between -45°F (-43°C) and 105°F (41°C) and vapor pressures which can range up to 125 psig (139.7 psia) at 70°F (21°C).[3/] The most commonly used liquefied gas propellants have a vapor pressure of 13.4 to 85 psia at 70°F (21°C) and boil below 70°F (21°C).[6/] A compressed gas, by Department of Transportation definition, has a vapor pressure which exceeds 25.3 psig at 70°F (21°C) or 89.3 psig at 130°F (54.4°C). In the aerosol industry, a propellant gas is considered a compressed gas if it has a vapor pressure above 125 psig at 70°F (21°C).[3/]

The liquefied gases are desirable propellants because they often also function as a self-pressurizing solvent in the aerosol formulation. They maintain a fairly constant pressure within the container throughout product use. In contrast, the compressed gas propellants do not function as solvents, and in addition, the internal container pressure drops as the product is used and the gas space increases. Presented below are general discussions of the liquefied and compressed gas propellants and the typical aerosol systems used for each.

a. The liquefied gas aerosol system:[1,6/] Liquefied gas propellants generally operate in either a two-phase or three-phase system depending upon the propellant. Each of these systems will be discussed separately.

(1) The two-phase system: In the two-phase system, the active ingredient is dissolved in the liquid propellant or a propellant/solvent mixture. The two-phase system is so termed because the propellant is

present in both the liquid and vapor state within the container. When the aerosol valve is opened, the vapor pressure of the propellant forces the active ingredient mixture through the valve, which in turn mechanically produces the spray.

Many of the "space sprays" (i.e., ultra-fine aerosol sprays) operate in the "two-phase" system. These products generally have 2 to 20% concentrate, containing the active ingredient, and 80 to 98% propellant. Pressure within the aerosol container is generally between 34.7 to 54.7 psia at 70°F (21°C) and spray particles range in size from less than 1 to 50 μ.

"Surface-coating sprays" also use the two-phase system, but in contrast to the space sprays, contain less low-boiling-point propellant (25 to 80% by weight) and more concentrate (20 to 75%). Particle size varies between 50 and 200 μ. Typical surface-coating sprays include hair sprays, residual insecticides, perfumes and colognes, paints and coatings, and topical sprays.

Current typical propellants of the two-phase spray systems include the chlorofluorocarbons or fluorocarbons F-11 (CCl_3F), F-12 (CCl_2F_2), F-114 ($CClF_2$-$CClF_2$), F-142b (CH_3CClF_2), and F-152a (CH_3-CHF_2).

(2) The three-phase system: Unlike the two-phase system, the three-phase system can use propellants not miscible with the liquid components of the aerosol formulation. The three-phase system consists of a liquefied propellant, a water solution of active ingredient, and a vapor phase. A fluorocarbon propellant is generally at the bottom of the water-active ingredient solution, while a hydrocarbon propellant floats on top.

The three-phase system is present either in a two-layer or a foam system. The two-layer three-phase system is further divided into an aqueous or a hydroalcoholic active ingredient solution. None of the propellant is introduced into the aqueous solution. The aerosol spray is produced exclusively by "mechanical" breakup in the actuator via constriction, valve orifice size, and tangential channels. Products of this type contain from 5 to 10% propellant, and have an internal pressure of 15 to 20 psig at 70°F (21°C); examples include moth-proofing sprays and many household cleaners. Hydroalcoholic solutions use a mixture of fluorocarbon and hydrocarbon propellants (e.g., butane, isobutane, and propane) which float on top of the active ingredient solution and are dispersed by shaking. Many insecticides and room deodorants contain hydroalcoholic active ingredient solutions.

The foam three-phase system generally uses 15% or less propellant (by weight) which is emulsified with the product. Most products use between 6 and 10% propellant and operate at 30 to 40 psig at 70°F (21°C).

Both hydrocarbon propellants and mixtures of F-114 and F-12 are commonly used to propel shave creams, shampoos, and some topical pharmaceuticals.

b. The compressed gas aerosol systems:[1,3,6] The compressed gas propellants have a much higher vapor pressure range, 500 to 1,000 psig (514.7 to 1,014.7 psia) at 70°F (21°C), than do the liquefied gas propellants. The two most common compressed gas propellants are nitrous oxide (N_2O) and carbon dioxide (CO_2).

Compressed gases dispense products in a solid stream, wet spray, or a foam. Because there is little or no reservoir of gas, when the contents of the aerosol unit are expelled, the volume of the vapor phase increases and the pressure drops. The solid-stream delivery system, which represents a very small portion of the market, may use nitrogen as the propellant. The nitrogen is both insoluble and immiscible with the concentrates which are generally in a semi-solid form. Products which at one time were dispensed by this system include dental creams, medicinal ointments and creams, cosmetic creams, vitamins, and some food products. Initial container pressure at 70°F (21°C) is between 90 and 100 psia.

Dispensers of most foam food products, (e.g., whipped creams and toppings) employ either nitrous oxide or carbon dioxide as the propellant; both are soluble in the concentrate.

Compressed gas spray dispensers use a mechanical breakup actuator to produce a wet spray. Choice of a compressed gas propellant depends upon the nature of the active ingredient solution and the compressed gas' potential reactivity with the active ingredient solution (e.g., CO_2 may form carbonic acid with water-based active ingredient solutions). Some medicinals in aqueous solutions, some residual insecticides, foods, and beverage concentrates are delivered by this system.

3. The chlorofluorocarbon and fluorocarbon propellants: Most chlorofluorocarbons and fluorocarbons are nonpolar, generally chemically inert compounds that maintain a nearly constant delivery pressure and a large expansion ratio. Chlorofluorocarbons are miscible with most nonpolar compounds and many are solvents over a wide range of temperatures. Due to the propellants' inertness, aerosol formulators need consider hydrolysis reactions which may form hydrochloric acid[6] and reactions that occur only under very specific circumstances, e.g., the reaction of F-11 with ethanol.

Chlorofluorocarbons most commonly used as aerosol propellants are F-11, F-12, and F-114. F-115 is used only in propelling food products. FC-318 (perfluorocyclobutane), previously used as a food propellant, is currently produced only in 100- or 1,000-lb batches and has almost completely been replaced by F-115 for economic reasons. Addition of the final fluorine molecule in producing FC-318 greatly increased the per-pound price. Du Pont estimates that, even at high volume production, FC-318 would still cost about $5.00/ lb.[7] For comparison of total fluorocarbon usage in aerosols and their price per pound, a summary of production and usage data is presented in Table IV-1.

Of the fluorocarbons listed in Table IV-1, only FC-318 is least suspect in the current ozone depletion controversy. Further discussion of this fluorocarbon, in addition to other candidate alternative fluorocarbon propellants, can be found in Section B of this chapter.

4. The chlorocarbon propellants: In the past, three chlorocarbons (methylene chloride, ethyl chloride, and vinyl chloride) have found limited use as aerosol propellants; most of the remaining chlorocarbons are not sufficiently volatile to function as propellants. In fact, methylene chloride is employed primarily as a solvent and/or vapor pressure depressant in aerosol formulations rather than as the propellant. In addition to methylene chloride, 1,1,1-trichloroethane (CH_3CCl_3) and perchloroethylene ($CCl_2{:}CCl_2$) have functioned as solvency constituents in aerosol formulations. Obviously, vinyl chloride is no longer used in propellant systems. The chlorocarbons are frequently used to replace or decrease the concentration of the more expensive F-11 in propellant blends for insecticides, hair sprays, and room deodorants.[3]

The feasibility and suitability of the chlorocarbons as alternative aerosol propellants are discussed in Section B of this chapter.

5. The hydrocarbon propellants: Hydrocarbons did not become important as aerosol propellants before 1954 because they were considered to be too flammable and to possess an unpleasant odor. However, in 1954 two events occurred which resulted in a rapid growth in the usage of hydrocarbon propellants. First, Risdon Manufacturing Company developed a valve which mechanically divided the product stream into a spray, and second, Phillips Petroleum offered bulk quantities of "Pure Grade" (with little or no odor) hydrocarbons. In addition, patent litigations encouraged many shave cream marketers to reinvestigate hydrocarbon propellants.[3] Thus, many heretofore chlorofluorocarbon-dominated markets were opened to hydrocarbon propellants.

By 1974, hydrocarbons were used in 45% of the approximately 3 billion aerosol units. In 1974, approximately 116 million pounds of hydrocarbons* were used as aerosol propellants. Hydrocarbons are used in approximately 87% of the nonpersonal product units. With the exception of shaving lathers (approximately 90% of which are hydrocarbon propelled), hydrocarbons are used only as constituents of propellant blends in personal product formulations. The hydrocarbon component cannot exceed 10% and maintain nonflammability of the propellant blend. The addition of 10% hydrocarbon and resultant reduction of the chlorofluorocarbon propellant lowers the cost of propellant per aerosol unit without adversely affecting spray characteristics.

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* MRI estimate based on data in Reference 3.

TABLE IV-1

USAGE OF FLUOROCARBONS IN AEROSOLS [7,8,9]

Fluorocarbon	Production 1974 (millions lb)	Percentage to Aerosols	Millions of Pounds to Aerosol	Price/ lb (¢)
F-11	347	82	285	38
F-12	509	60	305	42
F-114	27	95	26	49
F-115	NA[a]	10	-	51.6
FC-318	< 0.01	100	< 0.01	500

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[a] NA = Not available. F-115 production is included in the class "others." "Other" fluorocarbons include F-13, F-14, F-21, F-115, F-116, and others and had a 1974 production of 14 million pounds.

Three hydrocarbon propellants account almost exclusively for the 116 million pounds used in aerosols. Approximately 84% of the total is isobutane, 16% propane, and < 0.1% is n-butane. N-pentane and isopentane have only very limited uses, primarily as solvents or propellant extenders. They are both very volatile solvents, but do not have the necessary vapor pressures required of a propellant at ambient conditions.[3] (See Table IV-2 for physical properties.)

The hydrocarbon propellants may be utilized alone, in blends with other hydrocarbons, or in blends with chlorofluorocarbons. They have greater solubility and are much less expensive than the chlorofluorocarbon propellants. The hydrocarbons have a density of less than one, are not miscible with water, are not subject to hydrolysis, and are therefore useful in two-layer three-phase aerosol systems. They are generally very stable and react with halogens only under very severe conditions.[6]

In pure or aerosol grades, the hydrocarbon propellants are virtually odorless, colorless, and nontoxic. Liquefied hydrocarbons propellants have nearly constant delivery pressure and large expansion ratio, as do the fluorocarbons.[6] At the same weight percent of concentrate, the dispersive properties of the hydrocarbons are better than those of fluorocarbons.[3] However, they are not widely used in personal products because of their flammability and potential explosiveness in air. If a flame front forms within an enclosure, a rapid expansion of gases will sometimes cause an explosion.[3] An aqueous solution can effectively suppress the hydrocarbon's flammability and explosive potential; this fact and the lower cost explains why 90% of the shave lathers (an aqueous solution of active ingredient) are propelled by hydrocarbons. Hydrocarbons are also used to propel active ingredient solutions which are already flammable, formulated with some water, or not directed towards the body. Representative products include paints, shave lathers, shampoos, room deodorants, and household cleaners.[6]

The physical properties of the major and several alternative hydrocarbon propellants are shown in Table IV-2. A discussion of these propellants with respect to their feasiblity as replacements for F-11, F-12, F-114, and F-115 is presented in Section B of this chapter.

6. The compressed gas propellants: A propellant is often considered to be a compressed gas by aerosol scientists if the vapor pressure exceeds 125 psig at 70°F (21°C). For use in aerosols, a compressed gas is defined as a gas which can be liquefied only at very low temperatures or very high pressures.[3] The compressed gases have very little expansion power and therefore produce coarse, wet sprays. The initial pressure within the container is usually 90 psig (104.7 psia)[6] but drops as the product is used due to an increase in volume of the gas' vapor phase in the container's head space. Products often propelled by these inexpensive, nonflammable, nontoxic gases include windshield de-icers, furniture polishes, low-foam cleaners,

TABLE IV-2

PHYSICAL AND CHEMICAL PROPERTIES, TOXICITY AND REACTIVITY OF CANDIDATE AEROSOL PROPELLANTS[1,7,13-22]

Fluorocarbons Number	Formula	Boiling Point (°C/°F)	Vapor Pressure (psia)		Flammability[a] (% Vol. in Air)	Solubility		Hydrolysis in Water (g HCl/year)		Toxicity[b]	TLV (ppm)
			70°F (21°C)	130°F (54°C)		Water (25°C/77°F)	Alcohol (25°C/77°F)	Without Steel	With Steel Strips		
14	CF_4	-128/-198	-	-	None	0.0015 wt %	....	NA[c]	NA	6	NA
21	$CHCl_2F$	9/48	23	65	None	0.95 wt %		< 0.01 (86°F/ 30°C)	5.2 (86°F/ 30°C)	4-5	1,000
22	$CHClF_2$	-41/-41	138	312	None	0.13 wt %	....	< 0.01 (86°F/ 30°C)	0.1 (86°F/ 30°C)	5a	
23	CHF_3	-84/-119	618	-	None	75 cm^3/100 ml	394.5 cm^3/100 ml	0.005 (68°F/ 20°C)	-	6	
115	$CClF_2$-CF_3	-39/-38	120	267	None	0.006 wt %	Soluble	NA	NA	6	
116	CF_3-CF_3	-78/-109	445	-	None	Insoluble	....	0.005 (68°F/ 20°C)	0.05 (68°F/ 20°C)	6	
132a	$CHCl_2CHF_2$	58/136	3	13	None	751 ml/100 g	NA	NA	NA	NA	NA
133	CH_2ClCF_3	5/42	26	71	None	91 ml/100 g	NA	NA	NA	NA	NA
142b	CH_3CClF_2	-10/15	44	107	9.0-14.8			NA	NA	NA	
152a	CH_3CHF_2	-25/-13	76	191	5.1-17.1	....	....	NA	NA	6	NA
218	C_3F_8	-39/-38	-	-	None	0.5 ml/100 g	NA	0.001 (68°F/ 20°C)	0.04 (68°F/ 20°C)	NA	NA
227a	C_3HF_7	-26/-16	80	193	None	1.0 ml/100 g	NA	0.005 (68°F/ 20°C)	0.06 (68°F/ 20°C)	NA	
C318	C_4F_8	-6/22	40	107	None	0.5 ml/100 g	....	0.003 (68°F/ 20°C)	0.04 (68°F/ 20°C)	6	
502	Azeotrope 48.8% F22 51.2% F115	-46/-50	150	342	None	NA	NA	< 0.01 (68°F/ 20°C)	< 0.1 (68°F/ 20°C)	5a	
3110	C_4F_{10}	-2/-28	-	-	None	0.5 ml/100 g	NA	0.001 (68°F/ 20°C)	0.005 (68°F/ 20°C)	NA	
13B1	$CBrF_3$	-58/-72	214	449	None	0.0095 wt % (70°F/21°C)	....	NA	NA	6	1,000
Vinylidene fluoride	CH_2=CF_2	-86/-122	~ 530	-	NA	Slightly soluble	Soluble	NA	NA	NA	
Vinyl fluoride	CH_2=CHF	-72/-98	370	760	2.6-21.7	Insoluble	Soluble	NA	NA	NA	
Chlorocarbons											
Methyl chloride	CH_3Cl	-24/-11	74	174	7.6-19.0	400 cm^3/100 ml	3,500 cm^3/100 ml	NA	NA	4	100
Ethyl chloride	CH_3CH_2Cl	12/54	20	56	3.6-14.8	0.574 g/100 ml (20°C/68°F)	48.3 g/100 ml	NA	NA	4a	1,000
Vinyl chloride	CH_2=CHCl	-14/7	46	126	4.0-22.1	255 ml/100 g	Soluble	0.1 (68°F/ 20°C)	0.155 (68°F/ 20°C)		200
Methyl chloroform	CH_3CCl_3	74/165	2	7	None	Insoluble	Infinity	NA	NA	-	350
Methylene chloride	CH_2Cl_2	40/104	7	24	None	2 g/100 ml (20°C/68°F)	Infinity	NA	NA	4-5	500
Dichloroethylene	CHCl=CHCl	60/140	NA	NA	5.6-13.0	Slightly soluble	Soluble	NA	NA	-	200

TABLE IV-2 (Concluded)

Fluorocarbons Number	Formula	Boiling Point (°C/°F)	Vapor Pressure (psia)		Flammability[a] (% Vol. in Air)	Solubility		Hydrolysis in Water (g HCl/year)		Toxicity[b]	TLV (ppm)
			70°F (21°C)	130°F (54°C)		Water (25°C/77°F)	Alcohol (25°C/77°F)	Without Steel	With Steel Strips		
Hydrocarbons											
n-Butane	n-C_4H_{10}	-1/31	31	81	1.6-6.5	15 cm^3/100 ml (17°C/63°F)	1,813 cm^3/100 ml (17°C/63°F)	NA	NA	5	
Isobutane	i-C_4H_{10}	-12/11	45	110	1.8-8.[illegible]	13 cm^3/100 ml (17°C/63°F)	1,320 cm^3/100 ml (17°C/63°F)			5b	
Propane	C_3H_8	-42/-44	124	274	2.2-9.5	6.5 cm^3/100 ml (18°C/64°F)	790 cm^3/100 ml (17°C/63°F)			5b	1,000
Pentane	C_5H_{12}	36/97	8	27	1.4-8.3	0.03 g/100 ml (16°C/61°F)	Infinity	NA	NA		1,000
Isopentane	i-C_5H_{12}	28/82	12	34	1.4-8.3	Insoluble	Infinity	NA	NA		
Ethane	CH_3CH_3	-	555	-	2.6-10.5	10.2 ml/100 g	Slightly soluble	0	0		
Propylene	C_3H_6	-48/-54	171	387	2.0-11.0	Very soluble	Very soluble	NA	NA		
Compressed Gases											
Carbon dioxide	CO_2	-	757	-	None	8.2 ml/100 g	31 cm^3/100 cc (15°C/59°F)	NA	NA	5a	5,000
Nitrogen	N_2	-196/-320	-	-	None	60 ml/100 g	Slightly soluble	(68°F/20°C) very slight	(68°F/20°C) very slight	-	-
Nitrous oxide	N_2O	-88/-127	755	-	None	56.7 cm^3/100 cc	Soluble				
Sulfur dioxide	SO_2	-10/14	50	135	None	22.8 g/100 cc (0°C/32°F)	Soluble	-	-	1	5
Proprietary mixture[d]	-	NA	-	-	None	Soluble	Soluble	0	0	NA	3,000-4,000
Ethers											
Dimethyl ether	CH_3OCH_3	-25/-13	78	187	3.4-18.0	31.5 wt %	Soluble				
Vinyl methyl ether	CH_2=$CHOCH_3$	5/41	1,348	-	2.6-39.0	Slightly soluble	Very soluble				
Misc. Compounds											
Methyl formate	$C_2H_4O_2$	24/75	593	-	4.5-20.0	Slightly soluble	Slightly soluble	NA	NA	3	100
Ethyrylsulfur-pentafluoride	HC≡CSF_5	6/43	-	-	-	-	-	-	-	-	-

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a/ None = nonflammable compound.

b/ Underwaters' Laboratory Toxicity rating, 1 = most toxic, 6 = least toxic.

c/ NA = not available.

d/ Tabline Company, Berkeley, California.

engine cleaners, car waxes, residual insect sprays, dog-groomers, and food products such as whipped creams and toppings. Compressed-gas units account for approximately 5% of the aerosol sales.[4] Several once exclusively fluorocarbon-propelled products, e.g., hair spray, and now using carbon dioxide as the propellant, are currently being test-marketed.[9,10] Recent refinements in aerosol valves may make carbon dioxide systems viable for deodorants and some other personal products.[11]

Carbon dioxide and nitrous oxide are often used as a combination. The compressed gases are only rarely combined with the fluorocarbon propellants.[3] Chlorocarbons (such as methylene chloride and 1,1,1-trichloroethane) may be added to nitrous oxide to help compensate for pressure loss during product misuse, i.e., loss of the propellant if the actuator is depressed while the container is not upright. However, the chlorocarbon:N_2O mixture still produces a coarse spray.[1]

Compressed gas/liquefied propellant systems have also been considered. Either CO_2 or N_2O were used to pressurize the fluorocarbon propelled system to 90 psig (104.7 psia). The initial spray is finely divided but spray characteristics soon return to those of the liquefied system without the compressed gas. Thus, there is no advantage in superior spray characteristics or decrease in cost since the amount of liquefied propellant is not reduced.[1]

A discussion of the advantages, disadvantages, and technical feasibility of the compressed gases as alternative propellants is shown in Section B-3 of this chapter. A summary of physical properties occurs in Table IV-2.

B. Evaluation of Alternative Systems

To qualify as an aerosol propellant, a compound must possess certain physical and chemical characteristics. In addition, the environmental hazards, toxicity, manufacturing technology, and cost of the compound must be considered. A brief discussion of each of the above criteria is presented, followed by an initial compilation of candidates selected on the basis of physical characteristics only. From this initial compilation, candidates were eliminated on the basis of toxicity, incompatibility with active ingredient solutions, and/or potential environmental hazard. Lack of knowledge of the required manufacturing technology and high cost of the candidate propellant were not considered to be prime elimination criteria. Any compound considered to be a feasible aerosol propellant in terms of its physical, chemical, and toxicological properties was not eliminated from consideration. However, in some instances data are incomplete because of the compound's early developmental stages. Such data gaps will be noted in the brief discussion presented for each of the selected candidate propellants.

Aerosol units are classified into the following three types:

1. Personal products which include:
    - a. Hair care;
    - b. Antiperspirants and deodorants;
    - c. Medicinal and pharmaceutical;
    - d. Colognes and perfumes;
    - e. Shave lathers; and
    - f. Others.

2. Household products which include:
    - a. Room deodorants;
    - b. Cleaners;
    - c. Laundry products;
    - d. Waxes and polishes; and
    - e. Others

3. Other products which include:
    - a. Insecticides;
    - b. Coatings;
    - c. Industrial;
    - d. Food products and pan sprays;
    - e. Automotive;
    - f. Veterinary and pet; and
    - g. Others.

Personal products account for approximately 50% of all aerosol units, household products for 24% of the market, and all other products for 26% of the market. Of the personal products, 84% are currently propelled by fluorocarbons, while only 18 and 19% of household and all other products, respectively, are fluorocarbon propelled.[2,9,12]

Replacement of F-11, F-12, or F-114 in household and "all other" products should not present severe technical problems since these products are predominantly propelled by hydrocarbons, although some use chlorocarbons and compressed gases. In many instances, individual product types are exclusively nonfluorocarbon propelled.

The personal products represent the reverse situation. The shave lathers are the only product type not predominately fluorocarbon propelled. Consequently, alternative candidate propellants were selected to replace chlorofluorocarbons in the other personal product classes. Many of the initial candidate propellants were eliminated because they were not suitable for use in personal products, although they are currently used in other products.

1. Selection criteria for candidate propellents: Physical and chemical properties, consumer safety standards (i.e., low toxicity), environmental hazard, industry knowledge of required technology plus the cost of the propellant are all factors that must be considered by the aerosol industry in identifying candidate alternative propellants. This section presents the requirements and/or suitability ranges for each of these criteria.

a. Physical and chemical properties[1,3,7,13]

(1) Boiling point and vapor pressure: The boiling point of a liquefied gas propellant (or propellant blend) must generally fall between -45°F (-43°C) and 105°F (41°C) to achieve suitable aerosol performance. The vapor pressure of the liquefied propellant, or blends, should be between 10 to 70 psig (24.7 to 84.7 psia) at 70°F (21°C) for proper aerosol performance. Most viable propellants have a vapor pressure in the 20 to 50 psig (35 to 65 psia) range. Vapor pressures outside this range often give undesirable spray characteristics, or are not within the pressure limitations of the containers as defined by Department of Transportation regulations.

The vapor-pressure relationship with respect to temperature fluctuations must be considered to ensure adequate product performance. If, for example, the vapor pressure of a propellant drops to 20 to 30 psia at near freezing temperatures, it would not be a viable propellant for products such as windshield de-icers since internal container pressure would not be sufficient to expell the active ingredients. Conversely, should vapor pressure rapidly increase with temperature increase, storage in warm places may result in hazard as a result of overpressurizing of the container.

The vapor pressure of a liquefied gas propellant can be increased or reduced only by blending the propellants of varying vapor pressures or by the use of vapor pressure depressants. Reducing the amount of propellant per container is not effective in reducing internal pressure. The amount of propellant included in the aerosol formulation, for economic reasons, is generally near the minimum amount required to expell all the product unless an ultra-fine spray is required for optimum product performance.

(2) Flammability and explosiveness: Propellants for personal products are generally required to be nonflammable, nonexplosive, and nonsupportive of combustion. A flammable propellant can often be used in aqueous-based personal products because the water adequately suppresses the flammability. However, the combination of a hydrocarbon with an alcohol solvent, as in a hair spray, would greatly increase flammability and pose a potential hazard.

Flammability of a propellant (or propellant mixture) is determined on the basis of Department of Transportation and the New York City Fire Department standards. A flash point below 20°F (-7°C) (open cup test) is classified as extremely flammable; a flash point between 20°F (-7°C) and 100°F (38°C) (open cup test) is considered flammable. In addition, the Department of Transportation tests include a flame extension test and open and closed drum tests.

In general, hydrocarbon propellants are used when there is no increase in flammability hazard. The direction of the spray during the consumer use of the product is a factor. The product's flammability is of greater importance if the spray is directed towards the body than if the spray is directed away from the body, and is used either out-of-doors or in a well-ventilated area. There are no governmental regulations against the use of hydrocarbon propellants in personal products.

(3) Compatibility: A suitable propellant must be compatible not only with the active ingredient, but also with the container and valve. In many cases, incompatibility with the container can be resolved by either coating the inside or by inserting an impermeable container lining. Valve incompatibility can often be eliminated by redesign. However, no reactions should occur which may shorten the product's shelf-life or produce products that react with the aerosol formulation itself. Product stability tests are conducted at room temperature, 100°F (38°C) and 120°F (49°C) to assure a propellant's compatibility.

(4) Purity: Major propellants are available in 99%+ purity. Impurities can affect a product's odor and corrosiveness (and therefore shelf-life). A propellant used in most personal products must have a very high odor threshold, or the aesthetics of the products may no longer be acceptable.

b. Toxicity:[1,3,7/] A potential propellant must also have low toxicity, particularly for use in personal products. Before a propellant is utilized in consumer products, tests must be conducted to determine both acute toxicity (LC_{50}) and chronic toxicity. The acute toxicity of most common personal product propellants is generally several hundred or thousands parts per million, or greater than 20% in air, making them virtually nontoxic.

Of greater importance than the LC_{50} is the effect of long-term chronic inhalation of the propellant. A threshold limit value (TLV) or a time weighted average (TWA) must also be determined and shown to pose no long-term hazard. The fluorocarbon propellants usually have a TLV of 1,000 ppm. The consumer is typically exposed to between 10 and 400 ppm of the propellant during product use, depending on product type, mode of application, and location of use. This level rapidly declines to nondetectable amounts within seconds, and is always below TLV concentrations.

Also included in chronic toxicity is determination of the propellant's cardiac sensitization potential. Consumer misuse by deliberate propellant inhalation can result in exposures well above the 1,000 ppm level, i.e., 50,000 to 100,000 ppm. Under the stress conditions at which most misuse events occur (e.g., increased adrenalin, etc.), the level at which a propellant causes cardiac sensitization must be high enough that some margin of safety exists even under abuse situations.

In addition to low hazard in acute toxicity, chronic inhalation, and cardic sensitization potential tests, a propellant must also be nonmutagenic, noncarcinogenic and nonteratogenic.

c. Environmental hazard: On the basis of the current ozone-depletion theory, candidate propellants of very high atmospheric stability and a propensity for reaction with the ozone layer were considered to present a potential environmental hazard. Such compounds were thus not included in the selected list of candidate propellants.

d. Manufacturing technology and product cost:[7] For a propellant to be introduced to the aerosol market in a limited time (i.e., less than 5 years), a company must be familiar with its manufacturing technology. Development of a new propellant where there is no familiarity with the manufacturing technology requires at least 5 to 10 years, and possibly longer if raw materials are not available in bulk quantities.

The cost of the propellant is very important from a marketing standpoint, and is often closely linked to knowledge of the manufacturing technology.

Although not an elimination criterion in this report, inordinately high product cost and, to a lesser degree, ignorance of the needed manufacturing technology may result in abandonment of a propellant by the company.

2. Compilation of potential alternative propellants: Compilation of the initial list of candidate propellants was on the basis of physical properties only. Candidates for the list were assessed by consulting references on past and current aerosol technology,[1,3] industry technical bulletins,[13] and compendiums of physical and chemical properties.[14-17] Toxicology data[13,18-20] were also collected for later use as elimination parameters.

Table IV-2 presents the candidate propellants and summarizes their toxicity, reactivity, and physical and chemical properties.

3. Selected list of alternative propellants: The initial list of potential alternative propellants for personal product aerosol (see Table IV-2), was evaluated first by eliminating (on the basis of physical and

chemical properties) the unsuitable candidate propellants, secondly by identifying those candidates suitable for use in blends of aerosol propellants, thirdly by identifying candidates which may be technically and commercially feasible propellants in 5 to 10 years, and finally, by identifying those candidates that may be (both technically and commercially) suitable as personal product propellants within 5 years. As discussed previously (pp. 56 to 57), alternatives for nonpersonal product aerosol were not considered because (a) these products are currently available in mechanical delivery systems, and (b) approximately 82% of these products use propellants other than the chlorofluorocarbons.

Presented below is a discussion of the propellants in the four categories along with the criteria for including them in their respective categories.

a. Eliminated potential alternatives: Fifteen of the 39 candidate propellants were eliminated from consideration. It should again be noted that F-11, F-12, F-13, F-113, and F-114 were not considered for further usage in aerosols within the framework of this document because of their potential environmental threat.

To function as an aerosol propellant, a candidate must possess the suitable physical properties. The desirable vapor pressure range is 25 to 95 psia[3,7] at 70°F (21°C), however, a propellant can have an ambient vapor pressure up to 140 psia.[3] The boiling point of the compound should be between -45°F (-43°C) and 105°F (41°C). Seven of the 15 candidates were eliminated strictly on the basis of unsuitable physical properties (see Tables IV-2 and IV-3).

F-14, eliminated on the basis of unsuitable physical properties, also has a very long atmospheric residence, i.e., > 10 years. It is possible the F-14's high stability may lead to environmental problems in the future.

When using an aerosol product, the consumer may be exposed to from 10 to 400 ppm[7] of the propellant depending upon the product and the mode of use. Candidates which have a TLV of 400 ppm or less, are toxic by inhalation, or which pose a potential health hazard were also eliminated.

Candidate propellants were downgraded from consideration if, on the basis of the current ozone-depletion theory, they pose a potential environmental hazard. Compounds of this group are F-115, F-502 (an azeotrope of F-22 and F-115), and F-13B1.

The critical properties and boiling point of F-115 would make this compound a plausible candidate as a liquefied gas propellant. However,

TABLE IV-3

ELIMINATED CANDIDATE PROPELLANTS

	Elimination Criteria			
Propellant	Boiling Point	Vapor Pressure	Potential Reactivity With Ozone	Toxicity
F-14	Too low	Too high		
F-23	Too low	Too high		
F-115			Yes	
F-116	Too low	Too high		
F-502			Yes	
F-13B1	Too low	Too high	Yes	
Vinylidene Fluoride	Too low	Too high		
Vinyl Fluoride	Too low	Too high		May be toxic by inhalation
Vinyl Chloride				A carcinogen
Dichloroethylene				TLV 200 ppm
Sulfur Dioxide				TLV 5 ppm
Vinyl Methylether		Too high		
Methyl Formate		Too high		TLV 100 ppm
Ethynylsulfur Pentafluoride	-lack of data-			

the atmospheric residence of F-115 exceeds 10 years[9] and since F-115 contains chlorine and no hydrogen, it may be reactive with the ozone layer. F-502 contains 51.2% F-115 and the azeotrope would consequently have basically the same potential ozone reactivity as would pure F-115. F-13B1, the bromine analogue of F-13, was also downgraded as a candidate propellant. Bromine-containing compounds are more susceptible to photodecomposition than chlorine compounds. Since bromine radicals are as effective as chlorine radicals in terms of ozone scavenging, F-13B1 may also deplete the ozone layer.

Ethynylsulfur pentafluoride has been suggested as a possible aerosol propellant (Chemical Abstracts, 66, 1967, 55005y). The company that employed the inventor was contacted, but had no information on the candidate propellant.[7] Additional data sources[1,3,15-21] and later volumes of Chemical Abstracts were consulted, but no information was found. Ethynylsulfur pentafluoride could not be assessed as a potential propellant because of lack of data, and was therefore eliminated from consideration as a selected alternative candidate propellant. In addition, ethynylsulfur pentafluoride is probably too expensive for most uses.

The proprietary compressed mixture reportedly developed by Tabline Company, Berkeley, California,[23] was also eliminated from consideration as an alternative candidate propellant. Very limited data were available on the mixtures composition. It is said to have solubility in both alcohol and water which may present problems during product formulation. Thus, due to insufficient data (considered to be proprietary), this compressed gas system was eliminated from final consideration as an alternative. As additional data become available, this mixture may prove to be a viable alternative but no published information is available at this time.

The candidate propellants eliminated or downgraded from consideration are summarized in Table IV-3.

b. Candidates suitable as constituents of propellant blends for personal products: Fourteen of the candidate propellants were judged to be suitable as propellant-blend constituents. Many of these compounds are currently used as propellants for shave lathers, household, and other aerosol products. Several of these compounds are used as vapor-pressure depressants with some fluorocarbons, while others may serve a dual function of vapor depressant/solvent. This section presents a brief discussion of the chemicals included in this category. Numerical order does not indicate an order of preference.

(1) F-142b: This fluorocarbon is probably nontoxic (complete toxicological data are not currently available) and has ideal physical properties from the standpoint of a suitable aerosol propellant (see Table IV-2 for physical properties). F-142b is flammable at 9.0 to 14.8% volume in air. However, flash point tests showed F-142b not to flash even

to dryness.[1] Industry sources indicate that up to 60% F-142b, by weight, can be mixed with a nonflammable propellant without producing a flammable propellant blend.[7] F-142b may be excellent for use with several of the selected alternative fluorocarbons (see pp. 64 to 66) to produce blends with a wide range of vapor pressures.

(2) F-152a: F-152a has a higher vapor pressure than does F-142b, is nontoxic, and is slightly more flammable than F-142b (i.e., 5.1 to 17.1% volume in air). Mixtures of F-152a and nonflammable fluorocarbons would require relatively less F-152a than F-142b to maintain nonflammability. However, F-152a could be used in blends to produce a wide range of vapor pressures.[7] If the blend remains nonflammable, it is suitable as an alternative propellant system for personal products.

(3) n-Butane: n-Butane is very flammable (flash point -101°F (-74°C),[1] 1.6 to 6.8% volume in air flammability limits) but is nontoxic (Underwriters' Laboratory Class 5) and has suitable vapor pressure and boiling point properties. Its current volume of use in aerosol is not high, i.e., less than 0.1% of the total hydrocarbon aerosol propellants.[3] n-Butane is often used in blends with other hydrocarbons and may be used with nonflammable fluorocarbons. The blend can contain up to approximately 10% n-butane and remain nonflammable.

(4) Isobutane: A common propellant in nonpersonal products (and in shaving lathers), isobutane accounts for approximately 84% of all hydrocarbons used in aerosols.[3] A personal-product propellant blend with a nonflammable compound may contain up to 10% isobutane and remain nonflammable. A common blend of 45% F-11, 45% F-12, and 10% isobutane is currently used in many hair sprays without changing the spray characteristics produced by the more expensive 50:50, F-11/F-12 propellant mixture. There seems to be no technical reason why isobutane cannot be used in a similar manner with the selected alternative, nonflammable, fluorocarbons to produce a propellant blend suitable for use in personal products.

(5) Propane: Propane accounts for approximately 16% of the hydrocarbon propellant sales.[3] It has a high vapor pressure (124 psia, 70°F/21°C) under ambient conditions and may be excellent in blends with low vapor pressure fluorocarbons.

(6) n-Pentane: n-Pentane has a very low vapor pressure (8 psia at 70°F/21°C), is a good solvent, but is more flammable than either propane or isobutane. In amounts of less than 10% of the blend, n-pentane may serve as a vapor depressant/solvent in combination with nonflammable fluorocarbons.

(7) Isopentane: Isopentane has properties very similar to those of n-pentane although ambient vapor pressure is somewhat higher (12 psia at 70°F/21°C). Isopentane can feasibly function in the same mode in a propellant blend as can n-pentane.

(8) Propylene: This hydrocarbon is not commonly used as an aerosol propellant probably because of its high vapor pressure. Small amounts of propylene with a low vapor pressure propellant could possibly be used to produce a blend with a suitable vapor pressure.

(9) Ethane: Ethane is nontoxic but flammable. Ambient vapor pressure is very high, i.e., 555 psia. Small amounts of ethane may function as would propylene in a propellant blend.

(10) Dimethyl ether: Nonflammable propellant blends of 75% F-12, 10% F-11, and 15% dimethyl ether have been used in aerosol products.[1] It is technically feasible that dimethyl ether may be used with the selected alternative fluorocarbons to produce similar propellant blends.

(11) Ethyl chloride: This chlorocarbon is an extremely powerful elastomer solvent, is nontoxic (TLV = 1,000 ppm), has a low ambient vapor pressure (20 psia), hydrolyzes in water, and reacts with ethanol. It is currently used in propellant blends and mixtures as a solvent and can feasibly perform in the same manner with the selected alternative propellants.

(12) Methyl chloride: Methyl chloride is used in minute amounts in presently marketed aerosol units.[3,9] It is relatively toxic (TLV = 100 ppm) and may hydrolyze in the body to form methanol.[3] Methyl chloride can probably be used with the alternative propellants in a role analogous to its present use.

(13) Methyl chloroform: Methyl chloroform is nonflammable but is fairly toxic (TLV = 350 ppm). Because of its low vapor pressure, small amounts of methyl chloroform are presently used as a pressure depressant. It is possible that methyl chloroform can be used with alternative propellants in the role of a vapor-pressure depressant.

(14) Methylene chloride: Methylene chloride is also nonflammable, is less toxic than methyl chloroform, and does not hydrolyze to a significant extent in water. It is a very strong solvent and at high levels is a skin irritant. Methylene chloride can be used in small amounts as a combination vapor depressant/solvent with the alternative propellants.

c. Candidates that may be suitable aerosol propellants in 5 to 10 years: Five of the candidate propellants may serve as excellent alternatives in 5 to 10 years. These compounds, if currently available, are only produced in experimental quantities. Data in most cases are incomplete making difficult if not impossible analysis of technical feasibility as candidate aerosol propellants. In addition, complete toxicological data are not available.

Included among these compounds are the five following fluorocarbons: F-132a, F-133, F-227a, F-218, and F-3110. Table IV-2 may be consulted for a summary of available physical and chemical properties.

d. Candidate alternative propellants: There are six candidate propellants suitable for use as personal-product propellants. All these candidates are nonflammable, have a low order of toxicity, and can be available in sufficient quantities to meet market demands in less than 5 years.

It should again be noted that alternative propellants for nonpersonal products have not been considered. Many of the chemicals included among suitable blend constituents function as acceptable propellants alone, and could be used in nonpersonal products currently utilizing flammable propellants. However, as discussed previously in this report, 84% of the personal products are propelled by the fluorocarbons while only approximately 18% of the remaining aerosol products use fluorocarbons. The switch from 72 to 100% nonfluorocarbon propellants should offer no severe obstacles, unlike an 84% replacement required in personal products. Therefore, attention has been focused on identification of alternative personal-product propellants.

(1) F-21: F-21 is the first of the selected alternative propellants (consult Table IV-2 for properties). Some toxicological data are lacking, but these should be available by June 1976.* The manufacturers must then formulate products using F-21 and conduct 90-day inhalation studies. F-21 is a good solvent and may attack valves; however, industry feels this problem can be overcome with valve redesign.[7]

F-21 can also be made at a reasonable cost. Plants formerly producing F-11 and F-12 can be converted to products F-21 and F-22 with some capital investment (estimated to be about 15% of the current plant replacement value of $50 to $100 million).[7]

(2) F-22: F-22 can also serve as a suitable aerosol propellant. It can be blended with both F-142b and F-142a; blends of F-21 and F-22 may function as a replacement for F-11/F-12 blends.[7] F-22 currently has a very limited usage in aerosols, i.e., in flat-tire inflation cannisters.[24]

(3) FC-318: FC-318 has been used in the past as a food propellant and is approved as a food additive.[25] The vapor pressure at 70°F

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* A major manufacturer recently stated (February 1976) that toxicological data indicates F-21 probably is not acceptable as an aerosol propellant.

(21°C) is 40 psia; FC-318 could be blended with other fluorocarbons and blend candidates of higher vapor pressures to produce propellant blends with a wide range of ambient vapor pressures.

Although a technically feasible aerosol propellant, FC-318 may be hindered from a marketing standpoint because of a high cost per pound. Addition of the final fluorine and purification of the product are expensive processes (in both cost and energy). In addition, industry believes that existing plants cannot be converted, and that FC-318 would require new production facilities.7/

(4) Nitrous oxide (N_2O): N_2O is used in many food products, e.g., whipped creams and topping. Nitrous oxide was often used in combination with FC-318 in food products. At the low temperatures of refrigeration, FC-318 vapor pressure becomes so low that it no longer is an effective propellant. Pressurization with nitrous oxide helps to alleviate these problems encountered with low temperature storage.1/

Nitrous oxide is more soluble in the liquid phase of the aerosol formulation than is nitrogen; the higher solubility in chlorinated solvents results in smaller pressure drops and more latitude in the case of product misuse. A combination of methylene chloride, 1,1,1-trichloroethane and N_2O has been suggested for hair sprays. However, this system does have some undesirable characteristics. The aerosol spray is coarse. Perfuming products containing 1,1,1-trichloroethane may be difficult. Chlorinated solvents at high concentrations may be irritating to skin and adversely affect valve systems. As previously discussed, the internal pressure drops as the product is used in any compressed gas system. If the product is discharged in the improper position, the gas may be depleted before the product is fully utilized.1/

Since it is somewhat soluble in the aerosol formulation's liquid phase, N_2O tends to aerate the concentrates. N_2O is a good propellant for products requiring discharge as foam, aerated stream, or residual spray. Refinement of valve technology, as is being done with carbon dioxide, may allow further use of N_2O in personal products.

(5) Nitrogen: Nitrogen is insoluble in aerosol concentrations and allows no latitude for product misuse as do nitrous oxide and carbon dioxide. If the container is inverted during use, all of the nitrogen can be discharged making delivery of the product impossible.

Nitrogen is nontoxic, inert and inexpensive, but produces only very coarse sprays which are mechanically formed by the nozzle. There is also less product per container because the volume of the vapor phase must be increased above that required for liquefied gas propellants to insure that all of the product is discharged.1/ Redesign of valves or combinations of low vapor pressure fluorocarbons and nitrogen may be suitable for propelling personal products.

(6) Carbon dioxide: Carbon dioxide has been used as window cleaners, starch sprays, window de-icers, engine starters, and residual insect sprays where a coarse spray is desirable, or where spray droplet size is not highly related to effective product performance. However, recent refinements in valve design (i.e., mechanical breakup into a finer spray) have allowed test marketing of personal products once propelled only with fluorocarbons. A carbon dioxide propelled hair spray (Alberto-Culver's "TRESemme TWO") is now being test marketed.[10,26] CO_2 may also be a suitable propellant for deodorants.[10,11,27] One industry source thinks that CO_2 could be a viable propellant for one-fourth to one-third of the 3 billion aerosol units sold annually.[11]

Carbon dioxide is not a viable alternative propellant for every aerosol product. CO_2 can form carbonic acid in aqueous solutions. A fine mist of space-spray size (1 to 50 μ particles) has not yet been produced with CO_2 systems. Therefore, CO_2 is not yet a viable alternative for room deodorants, room insect sprays, antihistamines, asthma sprays, or paints and coatings.[11]

Carbon dioxide is much less expensive per aerosol unit than are the fluorocarbons. Only 5 to 20 g of CO_2 are required per unit to fully dispense the product, the cost of which is very low (~ 0.2¢/unit).[11] In addition, the average 16-oz unit CO_2-propelled contains about 20% more spray than does a 20-oz fluorocarbon propelled unit.[27]

Filling of CO_2 aerosol containers can be done using standard filling equipment with some minor adjustments. Estimates range from a low of approximately $9,000 (a conversion package currently sold by Chemetron Corporation)[11] to a high of $40,000 to $50,000[10] in additional equipment required to convert a typical aerosol filling line. However, one firm claims to save $3,000 a day packaging a CO_2 product than when it packaged the same product with fluorocarbon due to the difference in cost of the propellant. Product quality (percent fill) is checked by weighing units before instead of after adding the propellant, as is done with fluorocarbons.[28]

4. Mechanical alternatives: This section presents a discussion of both currently available and newly developed mechanical product delivery systems. Where data were available, estimates for current market size, system cost, and projected industry growth for the mechanical alternatives were included.

a. Systems requiring hand application

(1) Collapsible tubes: Collapsible tubes were in many cases the original form of product packaging for medicinals, shaving creams, and many food products. Many products sold as aerosols are still marketed in tubes. Of the total collapsible tube production in 1973 (~ 8 million gross), 27.8% were used for medicinals and pharmaceuticals and 1.2% for shaving creams. There were no food products packaged in tubes.[29]

Collapsible tubes are a viable mechanical alternative for many of the viscous products such as shave creams, hand creams, some cosmetic products, cheese spreads, and medicinal and veterinary ointments.

(2) Glass and plastic bottles: These products are a viable marketing system for hair products such as shampoos, setting lotions and conditioners, colognes and perfumes, household cleaners, waxes, and laundry products. The bottle was often the original form of product packaging.

The Modern Packaging Encyclopedia[29] and monthly issues of Modern Packaging, and Soap/Cosmetics/Chemical Specialties, were consulted for information on the market size of products offered in bottles which are also offered as aerosols. All data found were for total market size, e.g., 37.8% of all plastic bottles in 1973 were used for packaging household cleaners.[29] Estimation of the proportion of products also dispensed in aerosol form was not possible with this data. Consequently, although glass and plastic bottles are often viable alternatives, no estimation was made on their market magnitude.

(3) Creams, roll-ons, and sticks: These products were the original product form for deodorants and antiperspirants. Sales of these products in 1975 are above those in 1974. An industry source felt the dramatic increase in sales was due to the current ozone-depletion controversy, and that if the growth continued, the market could easily quadruple by 1978. Industry consumer sales in 1975 will probably exceed $25 million in creams and $45 million in roll-ons.[30]

Only deodorants have generally been offered in stick form, and one company is almost to the point where it cannot meet demands for this product. To broaden its scope, the same company is currently test marketing an antiperspirant in stick form.[30]

Many colognes are also offered in stick form. Estimations of the number of such products marketed in 1975 could be not obtained.

b. Barrier packs/bag-in-can, and piston containers: The barrier pack system consists of a metal container with an inner plastic bag that holds the product. A propellant is required, but is not mixed with the product. The product is loaded, using conventional filling equipment into the inner bag. A propellant is then loaded through the bottom of the can, surrounds the bag, and provides the dispersing force. The impermeable bag therefore functions as a barrier between the product and the propellant.[1,31,32]

Barrier packs were originally developed to dispense foods and other very viscous products such as creams, ointments, lotions, toothpastes, polishes, and cosmetic and pharmaceutical foams. The major bag-in-can systems include the "Sepro" can (Continental Can Company), the "Sterigard" dispenser (Sterigard Corporation), "Kang" (by Valois of France), "Power-Flo" (Sterigard Corporation), and "Cebal" (by Cebal of France).[1,31,32]

Another barrier pack type system is the piston container. The piston container is a metal can constructed around a polyethylene piston. The product is located above the piston; the propellant is inserted through the bottom of the can, and is located below the piston. Nitrogen as well as the other compressed gases function well in this system. This system is also only suitable for viscous products. Major piston containers include the "Mira-Flo" (American Can Company) and PTS, Pressure Tube System (Eyelet Specialty Company).[1,31]

The barrier pack systems are still in a developmental stage and, as far as one industry source knew, are marketed only on a test and experimental basis.[33]

A spring-loaded mechanical piston device has been announced in the media, but to the best of our knowledge, is still in a developmental stage with the areas of specific applicability not yet defined.

c. The bladder system: The bladder system is basically a barrier pack system, i.e., an impermeable bag within an outer rigid container. However, this system does not require a propellant, but instead uses the contracting force of the inner bag to dispense the product.

Kain's Research and Development Company has developed a bladder system called the Eco-Pure®. This system can disperse viscous products with a low-pressure inner liner, and insecticides, deodorants, hair sprays, disinfectants with a high-pressure inner liner. The cost of the Eco-Pure® system should be lower than conventional systems because there is no need for a propellant, and conventional containers and valves will require no redesign.[34]

Another bladder system (developed by Plant Industries, Inc.) termed SELVAC contains a two-layer inner membrane which functions as permeation barrier and pressure source. The first SELVAC system has a discharge pressure of 3 to 5 psi and is suitable for dispensing viscous products. A variety of containers can be used (glass, plastic, metal, cardboard) provided they are rigid.[35,36]

Within the last 6 months, a second SELVAC system has been developed that has a discharge pressure of 10 to 20 psi. Delivery pressures in this range would make the system suitable for many household products, deodorants, and perhaps antiperspirants. Sales of both SELVAC systems are estimated to be 1/2 million for 1975.[36]

Filling of bladder system units can be performed using conventional filling equipment, although a nominal amount of adaptor equipment may be required, the cost of which should not exceed $10,000.[36]

d. Mechanical spray pumps: Mechanical spray pumps have long been used in a wide range of products including household cleaners, insecticides, perfumes and colognes, medicinals, and hair care products such as setting lotions. In 1972, the first hair spray using a mechanical pump was marketed by Clairol.[37]

Today's market (1975) is estimated to be between 180[38] and 300 million units.[33,37,39,40] Of this market, 40% of the units are used in household products and insecticides, 10% in medicinal and pharmaceutical products, and 50% in hair care products, cosmetics, colognes, and perfumes.[38,40] The average mechanical spray pump costs about 10¢. However, sprayers used for a household product may cost only 7¢, while those used in hair care and cosmetic products may be priced from 13¢ to 15¢. Industry dollar volume by product type follows the same basic pattern.

The five leading manufacturers of mechanical spray pumps are: Calmar (Division of Diamond International Corporation); VCA/ARC (Dispenser Division of the Ethyl Corporation); Bakan Plastics (Division of Realex Corporation); Thiokol, The AFA Corporation; and Emson Pump Corporation.[41] One company plans to double its plant capacity by March 1976. Construction of entirely new production facilities is estimated to require approximately $10 million of capital investment for the space, tools, etc.[40]

C. Alternatives for Specific Use Areas

This section presents a discussion of the delivery systems which may function as viable alternatives for the personal products. Table II-5 presents a summary and relative viability ranking for all aerosol products by alternative system.

1. Hair spray: Hair sprays are currently marketed in mechanical delivery systems and as chlorofluorocarbon propelled aerosols. Presented below is a brief discussion of the mechanical systems and alternative propellants which may function as viable alternatives to the chlorofluorocarbon propellants in question (i.e., F-11, F-12, and F-114).

a. Mechanical alternatives: Hair sprays dispensed by mechanical spray pumps have been marketed since 1972.[37] Nearly every major hair spray marketer currently offers their product in both the fluorocarbon aerosol form and in mechanical pump form, indicating some consumer acceptance of the mechanical pump system. Criticism of the mechanical pump systems for hair spray with regard to leakage,[9] etc., may be over-stated. With regard to leakage, substantial improvements have been made in the pump systems. Packaging methods are essentially the same as for aerosol containers and thus are not a consideration as stated in a previous study.

The bladder system may feasibly function as a mechanical delivery system for hair spray. The manufacturer of Eco-Pure® suggests the high pressure inner membrane may provide sufficient internal pressure to propel a hair spray.[34] The newly developed SELVAC system may also be a feasible hair spray dispensing system.

b. Chemical and compressed gas propellants: Carbon dioxide propelled hair spray is currently being test-marketed by Alberto Culver.[26] Much industry attention has been directed toward technical refinement of valves, pressure drops, etc.,[10,11,33] and has increased the technical feasibility of CO_2 propellant usage in personal products.

Nitrous oxide is nonflammable, however, if can support combustion;[20] therefore it may not be suitable as a propellant in a product directed toward the face.

The selected fluorocarbons may serve as excellent alternative hair spray propellants. Combination of F-22 and hydrocarbons or other pressure depressants, such as ethanol, can feasibly replace F-11/F-12 blends commonly used in hair sprays. F-142b, at up to 60% of the blend, or F-152a could also be used in conjunction with F-21 (a major manufacturer recently stated (February 1976) that toxicological data indicates F-21 probably is not acceptable as an aerosol propellant), F-22, or possibly FC-318 in some applications. The low vapor pressure uncommon propellants such as F-132a could be used with F-22 as vapor depressants. There are many possible propellant blends achievable through combinations of chemicals included in the "candidates suitable as blend constituents" with the selected fluorocarbon propellants.

2. Antiperspirants and deodorants: Antiperspirants and deodorants are available in mechanical delivery systems and in aerosol form (using 100% chlorofluorocarbon propellants). The technically feasible mechanical delivery systems and alternative propellants are discussed below.

a. Mechanical alternatives: Cream, stick, and roll-on deodorants and antiperspirants are a major personal product market. All three delivery systems are suitable for both antiperspirants and deodorants. Consumer sales in 1975 are far above those of 1974, and may exceed $25 million for creams and $45 million for roll-ons.[30]

Mechanical spray pumps are technically feasible for delivering deodorants and antiperspirants and may prove to be aesthetically acceptable to the consumer. Tussey Cosmetics, affiliate of Lehnx and Fink Product Company, and Bristol Meyers ("Ban-Basic") currently offer a mechanical spray pump delivery system.

A final technically suitable alternative mechanical delivery system is the bladder system with the high pressure inner membrane. Both manufacturers feel this system is suitable for deodorants.[34,36] Many antiperspirants are powders which require the propellant as a carrier.[10,11] Products of this type would probably not be as suitable for use in the bladder system since no propellant is used.

b. Chemical and compressed gas propellants: Carbon dioxide is suitable only for delivering deodorant. Antiperspirants require the propellant as a carrier, and CO_2 cannot perform this function.[10,11] However, deodorants constitute a major portion of the approximately 620 aerosol deodorants and antiperspirants marketed in 1975 and CO_2 may be a technically feasible, nontoxic, nonflammable, inexpensive propellant.

Deodorants and antiperspirants are generally propelled by F-11/F-12 with very small amounts of F-114. Combinations of ethanol/F-22, F-22/F-142b (or F-152a), etc., may be a technically feasible propellants for deodorants and antiperspirants. Again, as with the hair spray systems, possible propellant combinations are numerous, and all have the characteristics required for use in personal products, i.e., they are nontoxic and nonflammable.

3. Shaving lathers: Shaving lathers are predominantly dispersed by systems other than aerosols using chlorofluorocarbon propellants. This section presents the viable mechanical alternatives and chemical propellants for delivering shave lathers.

a. Mechanical alternatives: Shaving lathers were originally available in collapsible tubes or as shaving lather bars/brush. In 1975, approximately 14 million* collapsible metal tubes were used for shaving lathers. Data on the number of shave-lather bars sold in 1975 are not available.

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* MRI estimate based on data in Reference 29.

Barrier packs and bladder systems designed for viscous products may be suitable for delivering nonfoamed shave lathers. Development of a foaming nozzle would increase the feasibility of the system for producing a foam having the similar characteristics as aerosol delivered shaving lather foams.

b. Chemical propellants: Over 90% of the currently marketed aerosol shave lathers are hydrocarbon propelled. The flammability of the hydrocarbons is suppressed to nonhazardous levels because the product is water based. About 10% of the propellants used in shave lathers are chlorofluorocarbons, but these are always used in small amounts with the hydrocarbons.[2,9] Discontinuing use of these fluorocarbons[9,10] in shave lathers will probably not require replacement by alternative fluorocarbons although these may technically function in this role. Therefore, since shave lathers currently use an "alternative" propellant, conversion to 100% alternative propellants should present no major obstacles for industry.

4. Perfumes and colognes: Perfumes and colognes can be delivered by both mechanical and aerosol systems. The viable alternatives are discussed below.

a. Mechanical alternatives: Perfumes and colognes are marketed in several alternative mechanical systems. Included are glass bottles, perfumed creams, solid, small roll-ons, atomizers, and mechanical spray pumps. All of these systems provide excellent product delivery, and since they require no propellant do not affect the odor in any way.

b. Chemical and compressed gas propellants: Carbon dioxide is odorless and nontoxic; data on the technical feasibility of delivering colognes and perfumes were not available although use may be possible.

The selected alternative fluorocarbons have a low order of toxicity and will provide suitable propellants for colognes and perfumes. A wide range of desirable vapor pressures can be produced by combining the various fluorocarbons such as ethanol/F-22, FC-318/F-22, F-142b/F-22, F-152a/F-22, etc., still maintaining propellant nonflammability necessary for products which contain alcohol solvents.

5. Medicinal and pharmaceutical products: Medicinal and pharmaceutical products are also available in aerosol and mechanical delivery systems. This section presents a discussion of currently marketed alternative systems and other viable alternative delivery systems. It should be noted that systems intended for use with medicinals and pharmaceuticals must come under FDA sanction.

a. Mechanical alternatives: Collapsible tubes provide an excellent delivery system for medicinal ointments. In 1973, 27.8% of 8.3 million gross collapsible tubes produced were used in packaging medinical and pharmaceutical products.[29]

Many medicinal products may also be dispensed by the barrier pack and bladder systems. The barrier pack and bladder systems with low-pressure inner liner were developed to accommodate viscous-type products. Since there is no contact between product active ingredient and the propellant, problems of chemical reactions with or combination of the product should not occur.

Delivery of medicinals requiring application as a spray may be possible with bladder systems equipped with high pressure inner liners and with mechanical spray pumps. Products such as local antiseptics, burn treatments, etc., can be effectively delivered by the 10 to 20 psi[36/] pressures produced by bladder systems with high-pressure inner liners. Mechanical sprayers already account for a major market, i.e., 18 to 30 million units in 1975 indicating satisfactory delivery and consumer acceptance.[33,38,40/]

b. Chemical and compressed gas propellants: Carbon dioxide generally produces a coarse spray; however, valve refinements and redesign are making possible finer sprays. As yet, ultra-fine sprays necessary for antihistamines and asthma sprays are not yet achievable with CO_2 units.[11/] Thus, only medicinal sprays (e.g., antiseptics) which provide satisfactory performance when applied in coarse sprays can at present use carbon dioxide as a propellant.

The selected fluorocarbon propellants will probably replace current use of F-11 and F-12 if these compounds are banned from use in aerosols. The selected fluorocarbons are nonflammable, inert (and thus should not affect the product) and nontoxic. Through combinations and blends, a wide range of vapor pressures are producible, and ultra-fine space-sprays required for certain products can be achieved.

6. Miscellaneous small-volume uses: A summary of the percentage of nonpersonal products propelled by fluorocarbons is presented in Table IV-4. Fluorocarbon use in these products can be replaced by hydrocarbons, compressed gases, or the selected fluorocarbons. Products not requiring space-spray fineness can be delivered by bladder systems with a high-pressure inner liner. The viscous food products such as cheeses can use the barrier pack systems, bladder systems with low-pressure inner liners, or collapsible tubes. These systems must have FDA approval. As discussed in Section B-4, "Mechanical alternatives," household products use 40% of the mechanical sprayers, i.e., 72 to 120 million units.[33,38,40/] Since fluorocarbons are not the predominant propellant and many of the products are currently available in mechanical alternatives, no major obstacles should be encountered if F-11 and F-12 are banned for use in these aerosols.

Table IV-5 presents a summary of the viable alternatives discussed for the five personal product types and for the smaller use volumes.

TABLE IV-4

PROPELLANT USAGE IN NONPERSONAL PRODUCT AEROSOLS[a,2,7,9]

Aerosol Product	Percentage Propelled By Fluorocarbons	Hydrocarbons	Compressed Gases
Household Products			
Room Deodorants and Disinfectants	20	80	-
Cleaners	10	90	-
Waxes and Polishes	30	70	< 1
Laundry Products	30	70	-
Others	10	90	-
All Other Products			
Coatings	5	95	-
Automotive	15	75	10
Insecticides	30	40	30
Industrial	50	50	-
Foods and Pan Sprays	25	5	70
Veterinary and Pet	50	50	-
Others	40	60	-

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[a] Some percentages are MRI estimates based on References 2, 9, and industry contacts.

TABLE IV-5

SUMMARY AND RELATIVE RANKING OF ALTERNATIVE DELIVERY SYSTEMS FOR AEROSOL PRODUCTS[a/]

		Mechanical Alternatives						Chemical Propellants				
					Bladder System							
Personal Products	Hand-Applied[b/]	Collapsible Tubes	Roll-Ons and Sticks	Barrier Packs	Low Pressure Inner Liner	High Pressure Inner Liner	Mechanical Pumps	Carbon Dioxide	Nitrogen	Nitrous Oxide	Hydrocarbons	Alternative Fluorocarbons
Hair Sprays	NA	NA	NA	NA	NA	NA	a	a	NA		c	b
Antiperspirants and Deodorants	a	b	a	NA	NA	b	a[b/]	b[b/]	NA	-	c	b
Medicinal and Pharmaceutical	a	a	c	b	b	b	a	b	c	-	a	b
Cologne and Perfume	a	-	a	-	-	b	a	b	c	-	c	b
Shave Lathers	a	a	NA	b	b	-	NA	NA	NA	NA	a	c
Household Products												
Room Deodorants	NA	NA	a	NA	NA	NA	b	b	NA	NA	a	b
Cleaners	a	a	NA	b	b	b	a	b	c	-	a	c
Laundry Products	b	-	NA	-	-	b	b	b	c	-	a	c
Waxes and Polishes	a	c	-	b	b	b	a	b	c	c	a	c
All Other Products												
Insecticides and Insect Repellants	NA	NA	b	-	-	b	a	a	c	-	a	c
Coatings	a	NA	NA	NA	NA	NA	NA	c	NA	-	a	c
Industrial	-	-	-	-	-	b	b	c	c	-	a	c
Foods and Pan Sprays	-	a	b	b	b	b	b	c[c/]	c	a	a	b
Automotive	a	-	-	-	-	b	b	a	c	-	a	c
Veterinary and Pet	a	a	c	b	b	b	a	b	c	-	a	b

[a/] Code: a - currently employed; b - not presently used, but definitely feasible; c - technically feasible, however, formulation problems may exist; dashes indicate utility and viability of the alternative is unknown; NA indicates the alternative is not applicable for the specified end-use product.

[b/] Hand-applied systems include creams, liquids in jars, and plastic bottles, etc.

[c/] Applicable for foods but not for pan sprays.

D. Production Data on Chemical Alternatives

This section presents production data (where available) and current manufacturers of the candidates suitable as blend constituents and as propellants as derived in Section B of this chapter.

1. Production estimates: The 1973 (or 1974 if available) productions of the alternative candidate propellants and the chemicals suitable as constituents of propellant blends are summarized in Table IV-6.

In 1974, only very small amounts of F-22 of the alternative fluorocarbons were used as aerosol propellants. Only a very small amount of the total F-22 production was used to propel aerosol products, i.e., the only product being flat-tire inflation cannisters.[24] FC-318 was not commercially produced in 1974 in anything but experimental quantities[7] but stock, from past production, was used to a minor extent (generally in combination with nitrous oxide) in food products. The remaining fluorocarbons in Table IV-6 are not currently used to propel aerosol products.

1974 use of hydrocarbon propellants is estimated to be 116 million pounds* divided between the three following chemicals: (a) propane - 19 million pounds; (b) isobutane - 97 million pounds; and (c) n-butane - < 0.1 million pounds. The remaining hydrocarbons are not presently used, or are used only to a very limited extent as aerosol propellants.

Fifteen percent (99 million pounds) of the total ethyl chloride was used as solvents or exported; 32 million pounds of methyl chloride went to solvents and exports; 47 million pounds of methyl chloroform were used in aerosols, solvents for adhesives, etc.; and 47 million pounds methylene chloride were used as solvents and vapor pressure depressants. The portion of each figure attributable to usage in aerosols only is not available.[9]

Production data for dimethyl ether and nitrous oxide were not available in literature sources consulted. The percentages of total nitrogen and carbon dioxide production used as aerosol propellants were not available.

2. Manufacturers of chemical propellants: Numerous manufacturers supply the chemical propellants (including the compressed gases). Many of the selected fluorocarbons are not yet available in commercial quantities. FC-318 is produced in 100 to 1,000 lb lots or is drawn from previous production supplies. F-132b, F-133a, F-218, F-227a, and F-3110 if available, are only in experimental supplies. F-22, and to a lesser degree F-142b and F-152a, are available in commercial quantities.[7]

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* MRI estimate based on Reference 3.

TABLE IV-6

ANNUAL PRODUCTION OF ALTERNATIVE CHEMICAL PROPELLANTS AND BLEND CONSTITUENTS[7,9,42,43]

Chemical	Production (millions of pounds) 1973	1974
F22	136	141
F21	12[a]	14[a]
F142b		
F152a		
FC-318		< 0.01
F132a	Experimental Quantities Only	Experimental Quantities Only
F133a		
F218		
F227a		
F3110		
Propane	9,068	
n-Butane	2,802	
Isobutane	1,092	
Pentane	[b]	
Isopentane	[b]	
Propylene	9,884	
Ethane	5,485	
Dimethyl Ether	NA[c]	
Ethyl chloride	660	660
Methyl chloride	544	458
Methyl chloroform	548	590
Methylene chloride	520	591
Nitrous oxide	NA[c]	
Nitrogen	16,380	
Carbon dioxide	2,770	

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a/ Individual production estimates are not available. This production figure is for other fluorocarbons which include F13, 14, 21, 115, 116, and others.

b/ 1973 Production of pentane, isopentane and all C_5 hydrocarbon mixtures is 493 million pounds.

c/ Production data are not available at this time.

A summary of the major manufacturers of chemical candidates suitable as blend constituents and candidates selected as alternative propellants is presented, by chemical compound, in Table IV-7.

TABLE IV-7

MANUFACTURERS OF PROPELLANT BLEND CONSTITUENTS AND ALTERNATIVE PROPELLANTS[43,44/]

Chemical	Producers
1. Fluorocarbons 21,22, 132b, 133a, 142b, 152a, 218, 227a, 3110	E. I. du Pont de Nemours and Company, Allied Chemical Corporation, Kaiser Aluminum and Chemical Corporation, Racon, Inc., and Union Carbide Corporation
2. Ethane	Allied Chemical Corporation, Atlantic Richfield Company, Dow Chemical Company, Exxon Chemical Company, Monsanto Company, Olin Corporation, Amoco Production Company, Phillips Petroleum Company, Puerto Rico Olefins, Mobil Chemical Company, Texaco, Inc., and National Distillers and Chemical Corporation, U.S. Industrial Chemicals Company Division
3. n-Butane	Atlantic Richfield Company, B. F. Goodrich Chemical Company, Commonwealth Oil and Refining Company, Inc., Coastal States Petrochemical Company, Olin Corporation, Amoco Production Company, Phillips Petroleum Company, Shell Oil Company, Mobile Chemical Company, Suntide Refining Company, Sun Oil Company, and U.S. Industrial Chemicals Company
4. Isobutane	Atlantic Richfield Company, B. F. Goodrich Chemical Company, Coastal States Petrochemical Company, El Paso Products Company, Olin Corporation, Amoco Production Company, Phillips Petroleum Company, Shell Oil Company, Sun Oil Company, and U.S. Industrial Chemicals Company
5. n-Pentane	Atlas Processing Company and Phillips Petroleum Company
6. Isopentane	Amoco Production Company and Phillips Petroleum Company
7. Propane	American Oil Company, Ashland Oil, Inc., Atlantic Richfield Company, Crown Central Petroleum Corporation, Commonwealth Oil and Refining Company, Inc., Commonwealth Petrochemicals, Inc., Cosden Oil and Chemical Corporation, Cities Service Oil Company, Coastal States Petrochemical Company, Exxon Chemical Company, Champlin Petroleum Company, Marathon Oil Company, Texas Refining Division, Olin Corporation, Amoco Production Company, Phillips Petroleum Company, Puerto Rico Olefins, Mobil Chemical Corporation, Suntide Refining Company, Charter International Oil Company, Sun Oil Company, Texaco, Inc., Union Oil Company of California, and U.S. Industrial Chemicals Company

TABLE IV-7 (concluded)

Chemical	Producers
8. Propylene	Amoco Chemicals Corporation, Allied Chemical Corporation, American Oil Company, Ashland Oil, Inc., B. F. Goodrich Chemical Company, Cities Service Company, Petrochemical Division, Chemplex Company, Cities Service Oil Company, Dow Chemical Company, E. I. du Pont de Nemours and Company, Inc., Eastman Kodak Company, Texas Eastman Company Division, El Paso Products Company, Gulf Oil Chemicals Company, Jefferson Chemical Company, Inc., Marathon Oil Company, Monsanto Company, Northern Petrochemical Company, Phillips Petroleum Company, Shell Oil Company, Standard Oil Company of Ohio, Mobil Chemical Company, Charter International Oil Company, Sun Oil Company, Texaco, Inc., and Union Carbide Corporation
9. Dimethyl ether	Chemical Solvents Corporation and Union Carbide Corporation
10. Ethyl chloride	American Chemical, Dow Chemical Company, E. I. du Pont de Nemours and Company, Inc., Ethyl Corporation, PPG, and Shell Oil Company
11. Methyl chloride	Allied Chemical Company, Conoco, Diamond Shamrock, Dow Chemical, Dow Corning, E. I. du Pont de Nemours and Company, Inc., Ethyl Corporation, General Electric, Stauffer, Union Carbide Corporation, and Vulcan Materials
12. Methyl chloroform	Dow Chemical Company, Ethyl Corporation, PPG, and Vulcan Materials
13. Methylene chloride	Allied Chemical Company, Diamond Shamrock, Dow Chemical Company, Dow Corning, E. I. du Pont de Nemours and Company, Inc., Stauffer, and Vulcan Materials
14. Nitrous oxide	Airco, Inc., Air Products and Chemicals, Inc., and Standard Air Company of New Jersey, Inc.
15. Nitrogen	50 Producers including Chemetron Corporation, Union Carbide, United States Steel Corporation
16. Carbon dioxide	63 Producers including Allied Chemical, Chemetron Corporation, E. I. du Pont de Nemours and Company, Inc., Kaiser Aluminum and Chemical Corporation

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V. FOAM BLOWING AGENTS

Fluorocarbons* are used in the manufacture of foams made from polyurethane, polystryene, and polyolefin. These compounds are primarily used as the blowing agents which form the cellular structure of these foams. Other type of plastic foams (primarily vinyl, urea, phenolic, and epoxy foams) are produced in much smaller quantities, and do not typically involve much usage of fluorocarbon blowing agents.

In 1974, approximately 78 million pounds of fluorocarbons were used in the production of plastic foams. This represents slightly more than 8% of total U.S. fluorocarbons production for that year. Rigid and flexible urethane foams together account for more than 90% of the fluorocarbon blowing agents in plastic foams. Rigid urethane foams consume twice as much fluorocarbons as do the flexible foams. Rigid urethane foams of low density, produced primarily for thermal insulation, use more than half of all fluorocarbons used as plastic foam blowing agents.

A. Major Types of Plastic Foams

Each of the commercially important plastic foams (flexible urethanes, rigid urethanes, polystyrene foams, and other plastic foams) have differing technical requirements and economic constraints on the blowing agents used. The resin systems, the production processes employed, and the end-use applications of these plastic foams currently dictate the choice of the type and quantity of blowing agents employed. To provide overall perspective before discussing the requirements for individual types and classes of foamed plastics, Table V-1 presents a summary of major types of plastic foams by process and application areas.

Each of the major foams systems currently employing fluorocarbon blowing agents will be discussed separately. A detailed treatment of the technology and chemistry involved in plastic foam production is beyond the scope of the present study; and has been addressed in recent surveys and reviews.[1-4]

Hence, the following discussion will emphasize those factors directly affecting the use of blowing agents, and the range of alternatives to be considered should it prove desirable to reduce fluorocarbon emissions from plastic foam manufacture.

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* The term fluorocarbon is used in this section to mean chlorofluorocarbon.

TABLE V-1

TYPES AND APPLICATIONS OF PLASTIC FOAMS

Type of Plastic Foam	Foam Production Process	Location of Foaming Operation	Blowing Agents Used	Typical Product Applications
Polyurethanes				
Low density rigid polyurethane (1.6 to 3.0 pcf)	- Pour (bun or continuous slab)	Plant	F-11, CO_2, F-113	Building panels, board stock, packaging, foam logs, pipe insulation
	- Cavity filling (pour or froth)	Plant or job site	F-11, CO_2, F-12, F-114	Refrigerators, boats, building walls
	- Spray on (spray or froth spray)	Job site	F-11 F-12, CO_2, F-114	Industrial tanks, pipelines, roofing
Medium density rigid polyurethane	- Pour, mold, cast	Plant	F-11, CO_2, F-114	Pattern stock, decorative shapes
Polyurethane structural foams (8.0 to 30.0 pcf)	- Mold, cast, reaction injection molding	Plant	CO_2, F-11, others	Furniture parts, industrial automotive parts
Flexible polyurethane foams	- Pour (bun or continuous slab) - Mold	Plant	CO_2, F-11, CH_2Cl_2	Auto seats, bedding, rug padding
Polystyrene				
Extruded film and sheet	- Extrusion from crystal	Plant	Pentane, F-12, others	Meat trays, egg cartons, packaging disposables
Expanded board stock	- Steam expansion to logs	Plant	Isopentane, pentane, CH_3Cl, hexane, F-12, others	Building insulation, flotation, packaging
Expanded shapes	- Bead board molding	Plant	Pentane, F-12, others	Cups, packaging, dunnage, molded board, foam parts
Polyolefin				
Medium density polyethylene	- Extrusion	Plant	F-114, F-12, F-11, others	Flotation, crash padding, packaging
Miscellaneous				
Phenolic foams	- Pour or slab	Plant or job site	CO_2, F-11, pentane	Building insulation, pipe insulation
Epoxy foams	- Pour, mold or syntactic	Plant	F-11, others	Specialty foams
Urea foams	- Foam gun	Plant or job site	Surfactant, CO_2	Mobile homes, building walls,
PVC plastesol foams, polyisocyanurate foams, polyester foams	- Various processes	Plant	F-11, others, organics	Specialty foams

B. Polyurethane Foams - Rigid and Flexible

1. Structure of the urethane foam industry: The structure of the industries that collectively are called the "plastic foam industry" varies substantially according to the resin involved. The complexity of industry structure increases markedly as the number of end uses and raw materials increases. The urethane foam industry is unusually complex and difficult to characterize because the urethane polymer does not come into existence until the foam is created, usually at the fabrication stage. The versatility of these foams has created numerous product forms, application methods, raw material types, competitive situations--and, therefore, corporate involvements. Three distinct segments make up the urethane foam industry: (a) the suppliers of basic raw materials and foam systems; (b) the fabricators and suppliers of flexible foam; and (c) the producers and fabricators of rigid foam.

a. Materials and systems: The major chemical producers and the chemical subsidiaries of other industries dominate the raw materials supply picture. Many of these raw materials suppliers, such as Olin and Goodyear, are forward-integrated into liquid urethane systems, broadly defined as packages of reactive components for ultimate conversion into foam. A number of intermediate-size chemical firms--Stepan, Reichhold, and Witco--supply urethane systems. The chemical divisions of other firms are also major suppliers of urethane systems. It should be emphasized that systems are most important to the rigid urethane foam industry, while the flexible foam fabricators generally purchase raw materials and formulate their own foams.

The suppliers of raw materials and systems are normally not engaged in fabrication, nor vice versa. Major exceptions to this rule include Upjohn and PPG Industries, both of whom supply systems and also engage in fabrication. Upjohn typifies those firms that are extensively vertically integrated. Figure V-1 portrays schematically the structure of the raw materials portions of the urethane industry.

b. Flexible urethane foam: Major production of flexible foams passes through a bun and slab stock fabrication stage. Almost all flexible foam producers rely on the basic raw materials. About half of the dashboard padding and cushioning used in the automotive industry are captively produced, employing urethane systems. The remainder is purchased principally from the tire and rubber companies who are large enough to produce their own flexible foam systems. The structure of the flexible foam producing industry with estimated material transfers is shown in Figure V-2.

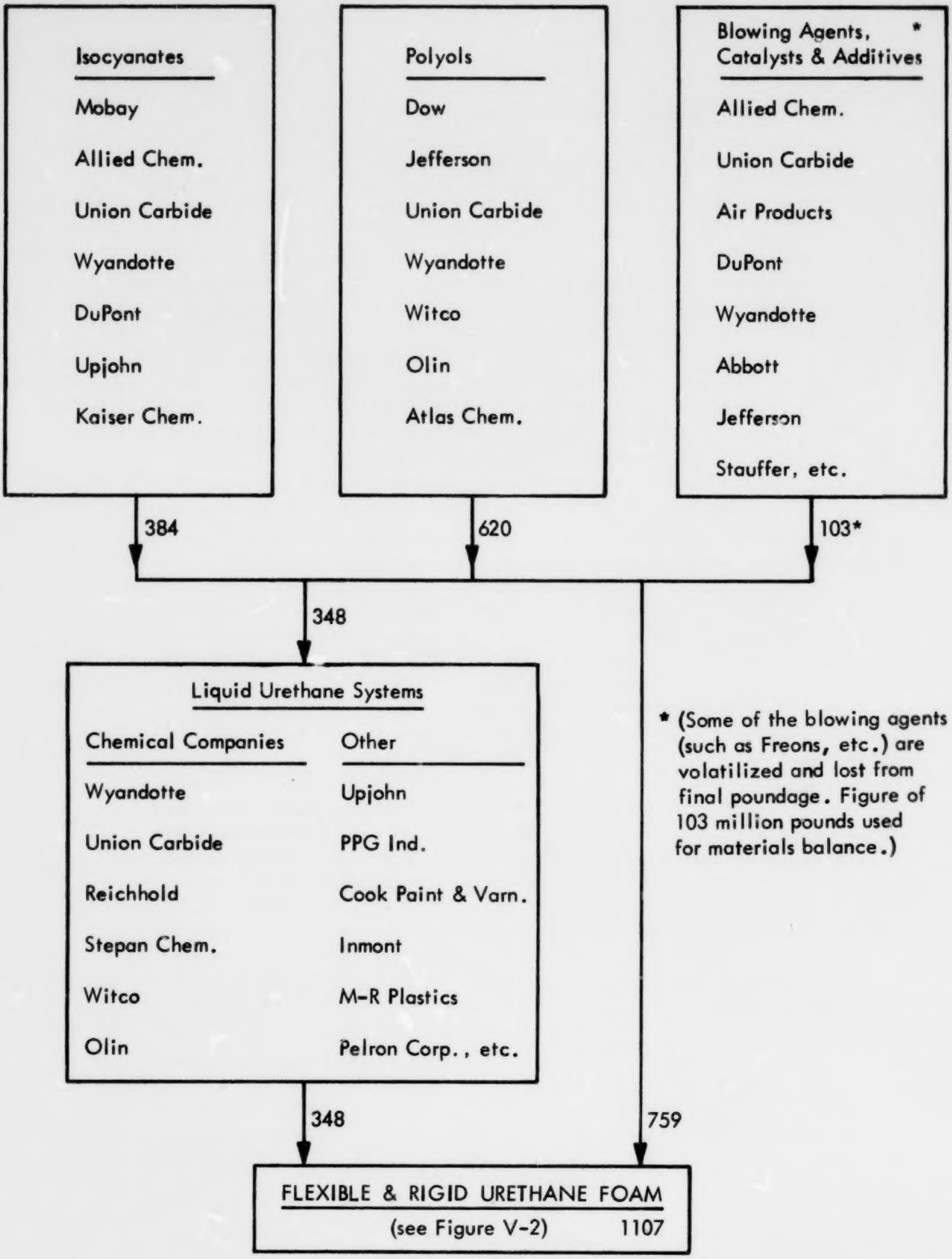
Isocyanates
Mobay
Allied Chem.
Union Carbide
Wyandotte
DuPont
Upjohn
Kaiser Chem.
Polyols
Dow
Jefferson
Union Carbide
Wyandotte
Witco
Olin
Atlas Chem.
Blowing Agents, Catalysts & Additives *
Allied Chem.
Union Carbide
Air Products
DuPont
Wyandotte
Abbott
Jefferson
Stauffer, etc.
384
620
103*
348
Liquid Urethane Systems
Chemical Companies
Wyandotte
Union Carbide
Reichhold
Stepan Chem.
Witco
Olin
Other
Upjohn
PPG Ind.
Cook Paint & Varn.
Inmont
M-R Plastics
Pelron Corp., etc.
* (Some of the blowing agents (such as Freons, etc.) are volatilized and lost from final poundage. Figure of 103 million pounds used for materials balance.)
348
759
FLEXIBLE & RIGID URETHANE FOAM
(see Figure V-2) 1107

Figure V-1 - Urethane Foam: Raw Materials Supply Structure
1972 Estimated Materials Flows, Million Pounds

Source: MRI 1974 Survey.

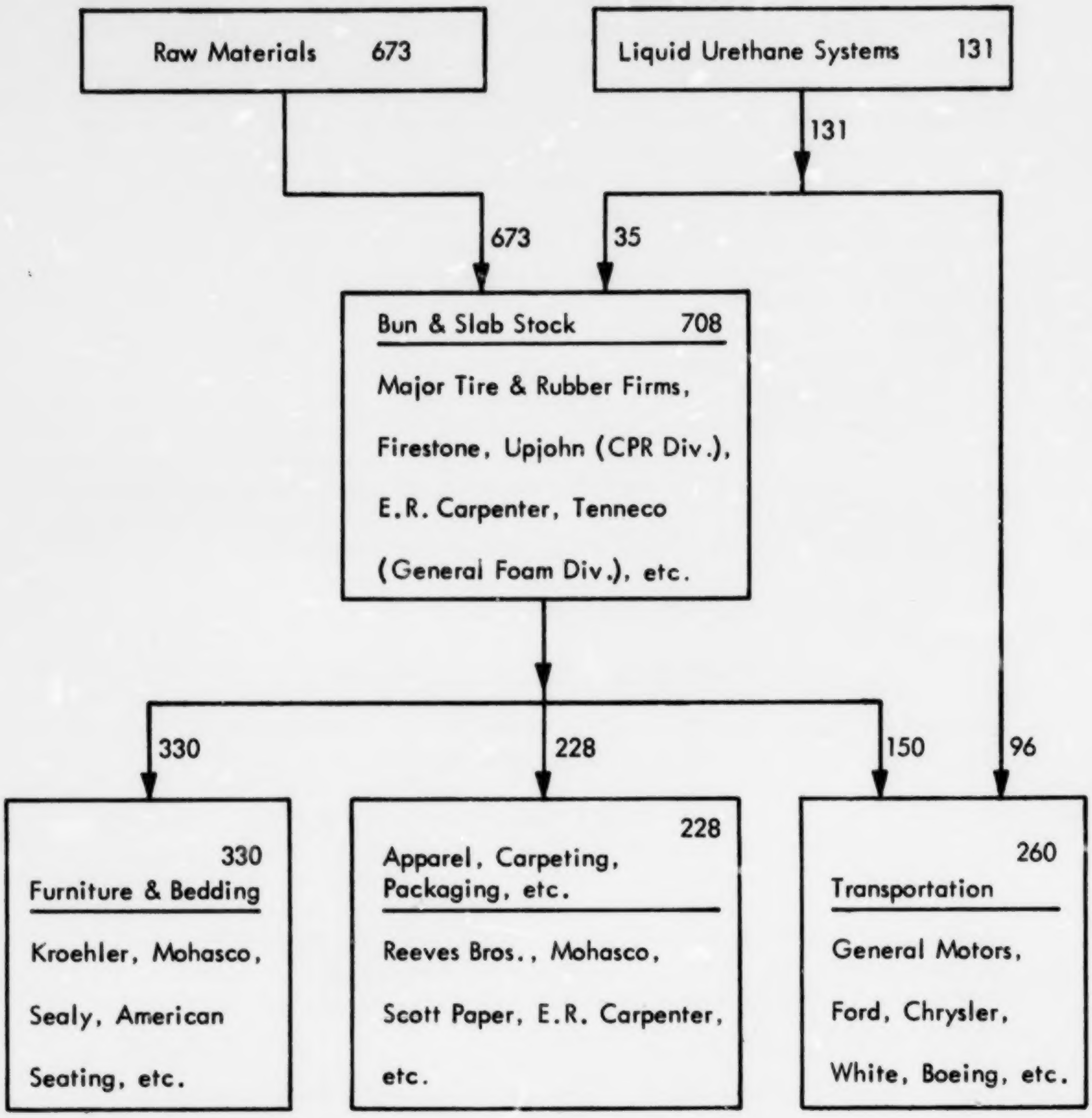
Raw Materials 673
Liquid Urethane Systems 131
131
673
35
Bun & Slab Stock 708
Major Tire & Rubber Firms, Firestone, Upjohn (CPR Div.), E.R. Carpenter, Tenneco (General Foam Div.), etc.
330
228
150
96
330 Furniture & Bedding
Kroehler, Mohasco, Sealy, American Seating, etc.
228 Apparel, Carpeting, Packaging, etc.
Reeves Bros., Mohasco, Scott Paper, E.R. Carpenter, etc.
260 Transportation
General Motors, Ford, Chrysler, White, Boeing, etc.

Figure V-2 - Flexible Urethane Foam Industry Structure
1972 Estimated Materials Flows, Million Pounds

Source: MRI 1974 Survey.

c. Rigid urethane foam: Fabrication originates from both raw materials producers and suppliers of liquid systems. This is because rigid foam is more diverse in application than flexible foam and there are literally hundreds of applicators and molders, each individually small, who find it more economical to purchase their materials in pre-engineered, prepackaged systems. At the same time rigid foam is growing rapidly in building insulation and structural foam parts for furniture. Consequently, many major producers of rigid foam board stock are the building materials suppliers. Because rigid urethane foam competes directly in insulation markets formerly dominated by rock wool and fiberglass, firms such as Owens-Corning Fiberglas are now among rigid foam producers. Most of the large refrigerator and appliance producers buy raw materials, while smaller appliance firms purchase systems. The transport carrier industry, makers of railroad freight cars and insulated truck trailers, rely totally on the purchase of foam systems. Furniture manufacturers purchase most foam structural parts from custom plastic processors, even though larger manufacturers have established their own foam production lines. Details of the rigid urethane foam industry structure are shown in Figure V-3.

2. Rigid urethane foams

a. Consumption of rigid polyurethane foams: Consumption of rigid polyurethane foams for all applications has been growing at a substantial rate over the past 10 years and is anticipated to show further growth through 1980 at nearly 10%/year.

By far the largest application of the rigid urethane foams is for thermal insulation. The most important application areas are in building construction, refrigerators, freezers, transportation carriers (truck trailers and freight cars) and industrial applications such as the insulation of tanks and pipelines. For insulation uses, urethane foams are typically produced at densities of 1.6 to 2.2 lb/ft^3 (pcf); and virtually all of the insulating foams employ fluorocarbon blowing agents.

Other uses of rigid urethane foams including packaging and dunnage, boats and flotation, and molded structural parts, may or may not employ fluorocarbon blowing agents. In particular, the medium to high density (8 to 26 lb/ft^3) rigid urethane moldings have grown rapidly in application between 1967 and the present. These molded parts replace wood in furniture, television cabinets, decorative interior profiles, and a variety of industrial parts. In the higher density ranges little or no fluorocarbon blowing agents are employed.

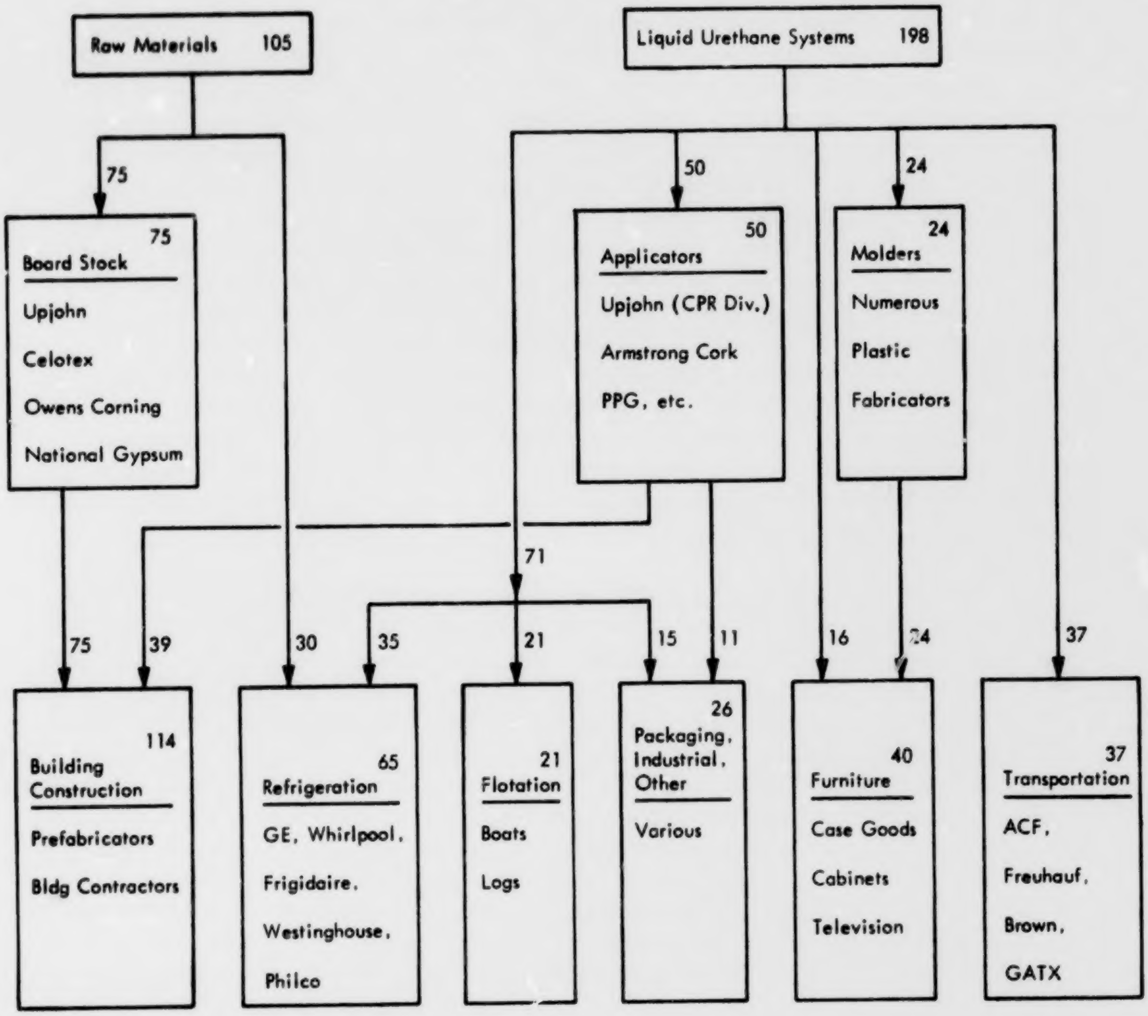
Raw Materials 105
Liquid Urethane Systems 198
75
50
24
75
Board Stock
Upjohn
Celotex
Owens Corning
National Gypsum
50
Applicators
Upjohn (CPR Div.)
Armstrong Cork
PPG, etc.
24
Molders
Numerous
Plastic
Fabricators
71
75
39
30
35
21
15
11
16
24
37
114
Building Construction
Prefabricators
Bldg Contractors
65
Refrigeration
GE, Whirlpool,
Frigidaire,
Westinghouse,
Philco
21
Flotation
Boats
Logs
26
Packaging, Industrial, Other
Various
40
Furniture
Case Goods
Cabinets
Television
37
Transportation
ACF,
Freuhauf,
Brown,
GATX

Figure V-3 - Rigid Urethane Foam Industry Structure
1972 Estimated Materials Flows, Million Pounds

Source: MRI 1974 Survey.

Table V-2 summarizes the statistics for rigid urethane consumption since 1965, with current estimates for 1980 consumption levels. Annual growth rates for the period 1973 through 1980 are also indicated. Total quantities of rigid urethane foams consumed are in reasonable agreement with the estimates of production reported by various trade sources. The breakdown of consumption by individual end applications is however subject to considerable variation depending upon the format used in reporting, and the variability of different trade reports. This table also includes an estimate of the quantity of rigid urethane foam blown with fluorocarbon agents. The basis of this estimate is the sum of thermal insulation plus a quantity of foam equivalent to that consumed in packaging and flotation uses. The industrial applications of rigid urethane foams are currently expanding at a rapid pace as a direct consequence of energy conservation programs. Trade sources predict that consumption for tank insulation, pipe lagging and insulated petroleum pipelines will exceed 30 million pounds by 1976, roughly double the consumption for 1974.

b. Rigid urethane foam production processes: There has been substantial technical change and progress in rigid foam making since the urethanes were first introduced from Germany at the close of World War II. The initial resin systems based on castor oil have been replaced by polyether and polyester types of urethane systems. Polyether foams such as those using sucrose-based polyols have been found to give properties very similar to the polyester foams but at a lower cost.[5-7] Systems based upon halogenated polyesters or phosphorous-containing polyols are widely used where maximum fire resistance is important. However, the polyether foams can also be rendered flame resistant by the incorporation of a suitable flame retardant. Blowing agent use with all types of resin systems is essentially similar. However, all foam formulations are sensitive to the choice and quantity of auxiliary blowing agent used. The use of different fluorocarbons or other volatile solvents will require adjustments in the silicone surfactant used to control cell size, and the water content of the resin system.

Rigid urethane foams are prepared by mixing two or more reactive liquid ingredients together. The chemical reaction which results forms a polymeric material which entraps gas bubbles to provide the desired cellular structure. The gas required for foaming is derived from carbon dioxide released during the polymerization reaction, or from the volatilization of an added blowing agent vaporized by the heat of reaction.

TABLE V-2

RIGID URETHANE FOAM CONSUMPTION
(Million Pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975(P)	1980(est)	Growth Rate 1980/1973(%)
Thermal Insulation													
Building Construction	17.0	24.5	31.7	47.5	58.0	71.2	83.3	113.7	150.1	154.2	175.0	275.0	9.0
Refrigeration Appliances	19.0	24.1	28.2	36.6	44.9	51.2	57.8	63.4	72.3	74.8	72.6	115.0	6.9
Transport Carriers	14.8	27.5	26.1	25.1	34.7	29.8	29.1	37.2	51.3	49.6	48.4	70.0	4.3
Industrial (tank and pipe)	3.0	5.0	7.0	8.0	12.0	12.1	10.5	10.0	11.0	15.8	15.4	33.0	17.0
Total Insulation	53.8	81.1	93.0	117.2	149.6	164.3	180.7	224.3	284.7	294.4	311.4	493.0	8.2
Other Applications													
Furniture	--	--	4.0	11.1	20.5	25.3	31.3	37.0	46.3	42.9	35.2	115.0	13.9
Packaging	1.0	4.0	5.0	6.0	8.0	7.2	6.0	7.0	9.1	12.1	13.2	30.0	18.5
Marine and Flotation	4.6	7.6	9.9	11.9	14.4	15.9[a]	11.2[a]	14.4[a]	15.4[a]	13.8[a]	13.2[a]	28.0[a]	8.9
Miscellaneous	7.0	13.0	16.0	9.0	15.0	26.2[b]	7.2[b]	7.0	6.9	8.1	8.8	17.0	13.7
Total Other	12.6	24.6	34.9	38.0	57.9	74.6	53.8	65.4	77.7	76.9	70.4	190.0	13.6
Total Rigid Urethane Foam	66.4	105.7	127.9	155.2	207.5	238.9	236.5	289.7	362.4	371.3	382.8	683.0	9.5
Quantity Reported by Trade	71.0	106.0	134.0	155.0	209.0	241.0	236.6	285.9	349.4	369.6	399.0	827.0	13.1
Fluorocarbon Blown Urethane Foam[c]	59.4	92.7	107.9	135.1	172.0	187.4	197.9	245.7	309.2	320.3	337.8	551.0	8.6
Percent Fluorocarbon Blown	89.5	87,7	84.4	87.0	82.9	78.4	83.7	84.8	85.3	86.2	88.2	80.5	

Source: MRI 1974 Survey updated 6-15-75.

Notes: [a] Due to changes in reporting format, the scope of industrial, miscellaneous and nonboat flotation varies; in some years foam logs were included with board stock; mine sealing foam not reported after 1972.

[b] Uses included in miscellaneous applications was reallocated for years subsequent to 1970.

[c] Fluorocarbon blown foam estimated to include all insulation applications plus the equivalent of flotation and packaging.

The liquid ingredients are mixed in a foam machine consisting of a pumping unit capable of accurately metering the components through a continuous mixer which blends the components uniformly. Preparation of the urethane system components, metering and complete mixing are all critical to the proper manufacture of polyurethane foams. Machinery for the proportioning and dispensing of urethane foams is highly developed, with equipment being offered by some 48 manufacturers. The basic forms and variations among commerically available urethane foaming machinery has been reviewed recently by Johnson,[87] and will not be considered in detail. After the mixture is dispensed from the metering and mixing head, the method of application, and the means used to contain the foaming mixture, differ widely according to the application. These factors in turn influence the choice of blowing agent and the formulation of the urethane system.

The four basic dispensing methods for rigid urethane foams are pour, froth, spray, and injection. Molding and casting are both generally considered as a form of foam pouring. The frothing process can be applied either to foam pouring, or froth spraying. Thus the basic dispensing methods can be divided into two broad classes--spraying and pouring. Rigid urethane foams can be manufactured by batch processes, by a continuous slab or "bun" process, by foaming or frothing in place, and by spraying.

In the U.S., the continuous slab production and foaming in place are the most common. Continuous production of rigid foam board stock (commonly used for building insulation) involves pouring the liquid mixture as a thin layer onto a continuously moving conveyor where it expands to form a continuous block of foam. After oven curing, the foam may be sliced to specific thicknesses by a variety of sawing methods. An alternative of increasing importance involves the continuous application of surface skins (paper, plastic films, or metal) with the panel expanding to standard thickness.

Foaming in place involves pouring the liquid mixture of foam components from the dispensing head directly into a cavity (such as the walls of a refrigerator or boat hull). The chemical reaction causes the blowing agent to expand, and the foam completely fills the cavity. Considerably accuracy and uniformity is required in dispensing the urethane into cavities and molds. Each volume of the liquid urethane expands 30 times in volume and therefore must be accurately measured and precisely placed within the mold or cavity in order to insure accurate filling, and avoid excessive pressure on the sides of the mold or product.

The froth process introduced in the early 1960's is being used to an increasing degree to minimize these problems. The frothing process involves the addition of another blowing agent, usually fluorocarbon-12 (alternatively, F-114 or F-115 may be used) injected directly into the mixing head. The mixing head operates at a pressure of about 100 psi to keep the frothing agent liquid until it emerges from the dispensing nozzle into the cavity or mold. The reaction and further expansion of the foam roughly doubles the froth volume, thus filling the cavity or mold without excessive pressures, and permitting more accurate filling of cavities.

Sprayed polyurethane foams are often used for on-site application of rigid thermal insulating foams. The liquid urethane ingredients emerge from the mixing head and are sprayed onto the desired surface to expand. As in pouring operations, froth spraying has become a convenient method of achieving the desired urethane thickness and maintaining control over the desired density and skin thickness.

The frothing pour process has become increasingly important for cavity and mold-filling applications. Refrigerators and freezers represent one of the most important applications of rigid froth pour-in-place foams. Thin-wall refrigerators can use approximately one-half the usual insulation thickness, thus resulting in up to 35% greater interior capacity. The average foam usage is 8 to 10 lb/unit. Froth foam is placed in the cavity between the refrigerator liner and the outer steel shell to bond the two surfaces together and completely fill the cavity.

When nonfrothed resins are used to generate foams of 2 lb/ft^2 density, complex jigs and supports must be used to contain the molds or sheets and prevent distortion during foaming. Pressures developed by foaming in cavities 1 to 2 in. thick may reach 2.5 to 3.8 psi on the walls of the mold, because of the high expansion ratio, and because about 5% excess urethane must be added to insure a complete foam fill.[9]

When froth poured foam is used, the foam expansion exerts only about 0.4 psi on the surrounding walls. Simple, flat walls on building panels or mobile homes and trailers require only minimum supports and jigs--usually plywood support is adequate. Refrigerator doors containing shelves, separators, and egg trays may require more complex jigs and fixtures. The foams have sufficient flowability to fill narrow and complex mold cavities such as thin shelves and egg frame protrusions of a vertically filled refrigerator door, but small holes must be positioned to allow the escape of air during the foaming process. These holes seal themselves as the foam gels.

c. Blowing agents in rigid urethane formulations: There are two general types of blowing agents used in the manufacture of urethane foams.

* Carbon dioxide generated in situ by the reaction of isocyanate with water.

* Auxiliary blowing agents--volatile liquids such as fluorocarbons, particularly trichlorofluoromethane, vaporized by the exothermic reaction between the isocyanate and hydroxyl components.

High-density foams are most frequently made using carbon dioxide (derived from organic additives) as the blowing agent, while low-density foams providing the best insulation properties are generally prepared using fluorocarbons for this purpose. For frothed foams, fluorocarbon-12 is used in addition to fluorocarbon-11.

Selection of the blowing agents in the foam formulation, and control over its vaporization directly affect foam density and thermal insulation effectiveness. Density influences most foam properties (strength, thermal, acoustical, electrical, and other properties). Therefore choice of the amount and type of blowing agent is one of the most important controls for foam properties. The effect of water and fluorocarbon-11 concentration on foam density is shown in Figures V-4 and V-5.[10/]

The most significant difference resulting from the selection of either carbon dioxide or fluorocarbon as blowing agent lies in the thermal insulation effectiveness. If the cell size and shape, and the percentage of closed cells are the same, the K factor (initial) of fluorocarbon-11-blown foams is 0.10 to 0.15, while that of CO_2-blown foams is 0.22 and 0.24. This difference in K factor is quite evident when comparing the thermal conductivities of cut, rigid polyester urethane foam specimens.[11/] The lower K factor for fluorocarbon-blown foams means that the amount of insulating material needed for a given application may be reduced by as much as 50%.

The nature of the blowing agent also influences electrical properties. When water is used to generate carbon dioxide, water vapor may become entrapped within the cells and subsequently absorbed by the polymer increasing its dielectric constant and dissipation factor. Water in the foam, from any source increases the absorption of RF radiation at radar frequencies. In reproducing rigid foams for radomes and microwave applications, special precautions are taken to minimize the presence of water in the foam.

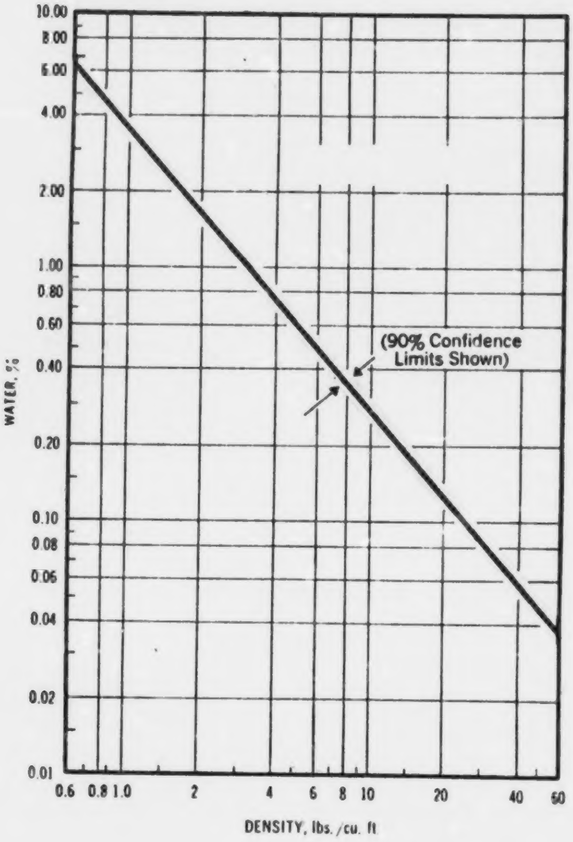

Figure V-4 - Effect of Water Concentration on Foam Density

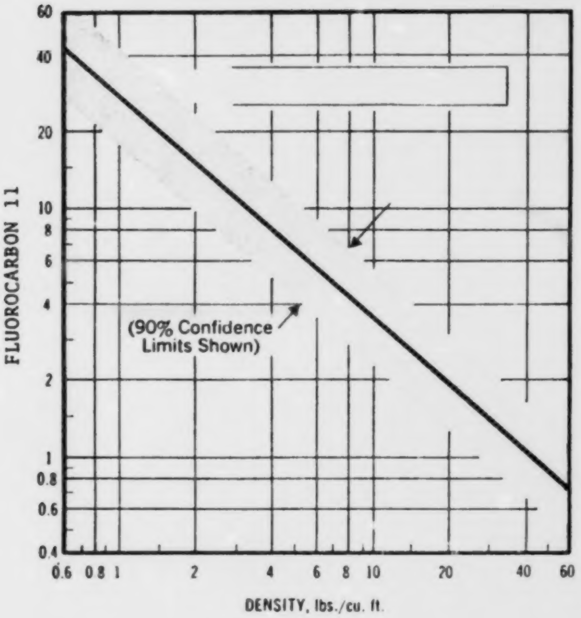

Figure V-5 - Effect of Fluorocarbon-11 Concentration on Foam Density

Thus, combinations of water and fluorocarbon blowing agents are used in different types of rigid urethane foam depending upon the application. Table V-3 gives typical starting formulations for rigid urethane foam systems intended for different applications. The total fluorocarbon content of these urethane systems ranges from less than 1% up to 17% by weight. Low-density foams for thermal insulation represent 80% of total output. The fluorocarbon content of systems for thermal insulation foams more typically is between 12 and 16% by weight.

d. Effect of blowing agents on thermal properties of foam: More than 80% of rigid urethane foams are produced for thermal insulating applications. Achieving and maintaining the lowest practical thermal conductivity (K value) is of critical importance since the quantity of insulating foam required increases directly with thermal conductivity.

In low density plastic foams, the thermal conductivity of the gas within the cells is, of course, the controlling factor determining the conductivity of the foam. The cell gases make up about 97% of the total volume of the foam, while the resin network makes up only 3% of the foam. The thermal conductivity of the gas depends upon the gas composition, and the gas composition is often hard to define. Carbon dioxide blown foams initially contain nearly pure CO_2 within the cells. But CO_2 diffuses readily through urethane, and much or all of the initial CO_2 in the foam cells will eventually be replaced by air.

The low thermal conductivity of halocarbon vapors, coupled with relatively slow diffusion through urethane resin is largely responsible for the nearly universal use of fluorocarbon blowing agents in preparing urethane insulating foams. The relationships between foam density, cell size, composition of the vapor in the cells, structural variables, and aging effects on thermal properties has been intensively studied for more than 20 years.

In order to understand the effect of blowing agents on thermal conductivity of foams, it is useful to separate the components of heat transfer through a foam structure. While more elaborate and complex expressions have been developed,[12-15] thermal conductivity may be considered as:

$$K = k'_s + k'_g + k'_r + k'_c \qquad (1)$$

TABLE V-3

TYPICAL RIGID URETHANE FOAM SYSTEMS

Ingredient (Parts by wt)	Type of Rigid Foam					
	Continuous Slab Stock Polyether	2.0 pcf Board Flame Resistant Polyether	1.4 pcf Insulation Flame Resistant Polyether	Halogenated Polyester Flame Resistant	1.6 pcf Frothed Polyether	12.0 pcf Structural Foam Molding
Polyol	100.0	70.0	70.0	-	100.0	115.5
Polyester	-	-	-	100.0 (Br)	-	-
Flame retardant	-	30.0	30.0	-	-	-
Isocyanate	46.0	108.0	108.0	92.0	78	132.0
Surfactant	1.0	1.0	1.0	2.0	1.2	0.02
Catalyst	0.2	1.5	1.5	0.5	0.65	15.0
Catalyst diluent	-	1.5	1.5	-	-	-
Water	3.6	-	-	-	-	-
Fluorocarbon F-11	16.0	30.0	40.0	35.0	25.0	2.0
Other blowing agent	-	3.0(F-113)	-	-	12.0 (F-12)	-
Total	166.8	245.0	252.0	229.5	217.9	264.5
% Fluorocarbon by weight	9.6%	13.5%	15.9%	15.3%	17.0%	0.76%

where K = the thermal conductivity of the foam in Btu/(hr)(ft^2)(°F/in)

k'_s = conductivity through the polymer network of the foam

k'_g = thermal conductivity of the gas within the cells

k'_r = the component due to thermal radiation through foam

k'_c = the component due to connection within the foam

As a good first approximation[16] for low density foams, heat conduction through the solid and gas phases can be expressed as the product of the thermal conductivity of each phase times its volume fraction. Solid urethane polymers exhibit K values ranging from 0.7 to 2.0; with a typical value of 0.9 to 1.0. Thus, the conductivity through a foam containing 3% urethane would be about:

$$k'_s = 0.03 \times 0.9 = 0.027 \text{ K units}$$

Similarly, the conductivity through the cell gases would be: $k'_g = 0.97 \times$ K value of the gas. Table V-4 gives thermal conductivity values for some of the gases found in urethane foams. It can be seen that the values for halocarbon vapors are considerably lower than those of air, nitrogen or carbon dioxide.

Foam producers wish to use blowing agents that measurably reduce the effective K value of the insulating foam. However, the blowing agent gases within foam cells are not normally pure halocarbon vapors, and the composition of these gases changes over time altering the thermal conductivity of the foams. The thermal conductivity of gaseous mixtures can be approximated as:

$$k_m = N_1 k_1 + N_2 k_2 \qquad (2)$$

where k_m = the conductivity of the mixture

N_1 and N_2 = the molfractions of gases 1 and 2

k_1 and k_2 = the respective conductivities of the pure gases

TABLE V-4

THERMAL CONDUCTIVITY OF BLOWING AGENT VAPORS[17-19]

Gas or Vapor	Thermal Conductivity, k_g (Btu/(hr)(ft^2)(°F/in)) 32°F	77°F
Carbon Tetrachloride	0.0384	0.0450
Chloroform	0.0456	0.0516
Methylene Chloride	0.0468	0.0540
F-11	0.0468	0.0575
F-12	0.0576	0.0660
F-21	-	0.068 (at 86°F)
Benzene	0.0624	-
Methyl Chloride	0.0636	0.0738
Acetone	0.0684	-
F-114	-	0.0770 (at 86°F)
Methyl Acetate	0.0708	-
F-22	-	0.0806 (at 86°F)
Iso-Pentane	0.0864	0.0996
Carbon Dioxide	0.1020	0.1156
Nitrogen	0.168	-
Oxygen	0.170	-
Air	0.168	0.181

When cured foams are aged exposed to air, the K factor is degraded by migration of gases such as O_2, N_2, H_2O (vapor) and possibly some CO_2 into the foam.* Unless the foams are protected by surface skins or other barriers, this dilution of the fluorcarbon vapors within the cells will eventually result in poorer insulating value. Producers of foams are attempting to develop foams which retain their initial low K factor. A comparison of conventional foams and experimental foams, and self-skinning sprayed foams on aging in air is shown in Table V-5.[20] If the foam is contained within a sealed cavity (refrigerator cabinet, or building panel) or if the thick polymeric skin is left on the foam surface (as usually happens with sprayed foams), there will be relatively little change in composition of the gases within the foam. Cut and oven-aged board stock, on the other hand, undergoes a significant change in thermal properties as a result of diffusion.

The effect of using different blowing agents on the thermal conductivity or urethane foams can be estimated with reasonable accuracy. Experimental values generally agree within 5 to 10% of K values calculated by various mathematical approximations.[21] It is more difficult to predict the extent and rate of gaseous diffusion and change in K value that will occur during aging if nonfluorocarbon blowing agents are used. The present state of knowledge about the diffusion of organic vapors through foam structures is not adequate[22] to anticipate how such materials would behave over time.

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* Note: There are two reasons that atmospheric gases initially diffuse into the foam, diluting the fluorocarbon vapors rather than diffusion of the FC out of the foam cells.

1. The diffusion rate constants for fluorocarbon vapors through urethanes are much lower than those of oxygen or nitrogen, and nearly 100-fold lower than that for CO_2. The rate of loss of the large, heavy fluorocarbon molecules by diffusion from foams is quite low.
2. Gaseous pressure within the cells of rigid foams after cooling is considerably below atmospheric pressure. Unless the compressive strength of the foam is adequate, chilling the foam may result in it being crushed by air pressure.

	Diffusion Constant (cm^2/sec)
Oxygen	1.12×10^{-7}
Nitrogen	6.27×10^{-8}
F-11	2.25×10^{-9}

TABLE V-5[20/]

CHANGE IN K-FACTOR OF FOAMS ON AGING

(Cut surfaces exposed to air at 68° F;
K in Btu/(hr)(ft^2)(° F/in)

Foam Type	K Initial	K Aged 10 Days	K Aged 120 Days
Conventional Foams			
Standard Commercial F-11 Blown	0.120	0.150	0.165
Commercial Foam Supplier A	0.120	0.140	0.158
Commercial Foam Supplier C	0.120	0.154	0.159
Experimental Foams			
Experimental J	0.115	0.138	0.153
Experimental N	0.100	0.129	0.139
Experimental O	0.101	0.120	0.138
Experimental P	0.105	0.123	0.133
Foams Sprayed On			
Wood at 2.01 lb/ft^3 (Core 1.86 lb/ft^3)	0.105	0.140	-
Steel at 2.07 lb/ft^3 (Core 1.84 lb/ft^3)	0.103	0.131	-
Aluminum at 2.06 lb/ft^3 (Core 1.92 lb/ft^3)	0.104	0.137	-

Despite these limitations, the effect of various blowing agents on thermal conductivity of urethane foams has been estimated for a few simple systems in order to show the magnitude of differences in thermal properties. Table V-6 compares the K values computed from Eqs. (1) and (2), using data from Table V-4 for vapor conductivities of blowing agents. Calculated values are generally in agreement with reported thermal conductivities of freshly prepared or 1-day aged foams. The results of cellular gas analysis studies on rigid urethane bun stock are shown in Table V-7.

It can be seen that air, carbon dioxide and most hydrocarbons are not capable of providing the desired low K values in urethane foams. For insulating use within the temperature range of 0 to 150°F, some halogenated hydrocarbons are theoretically able to contribute low thermal conductivity to foams. However, any such alternative blowing agent would also have to satisfy other important criteria--such as compatability with the formulation, effect on foam formation, effect on foam properties and aging, acceptable flammability, toxicity, etc.

At lower temperatures (below about -10°F) it has been reported that F-12 is markedly superior to the other fluorocarbons, and may offer lower thermal conductivity than any other blowing agents.[15/]

3. Flexible urethane foams

a. Consumption of flexible urethane foams: Flexible urethane foams are produced primarily for cushioning, textiles and carpet underlay applications. Table V-8 shows recent trends in consumption of flexible urethane foams for each of the major end uses. Because the largest uses depend upon automotive sales and home furnishings, growth in flexible foams is more sensitive to the state of the U.S. economy than is the case with rigid foams.

b. Production technology for flexible urethane foams: The technology and chemistry involved in producing flexible urethanes is quite similar to that for rigid foams. Despite these similarities, the manufacture of flexible foams has become a highly specialized segment of the industry, usually separate from the production of rigid urethane foams. The principal differences in production and marketing which characterize flexible urethanes versus rigid foams include:

TABLE V-6

EFFECT OF BLOWING AGENTS ON THERMAL CONDUCTIVITY

Computed and Experimental K-Values for 2.0 lb/ft^3 Urethane Foams

* At 2.0 lb/ft^3 foam is 3% polymer; 97% gas by volume

* Radiation component $k'_r = 0.02$; convection $k'_c = 0$

* Solid urethane polymer $k_s = 0.924$; $k'_s = 0.03 \times 0.924$ or 0.0277

Blowing Agent Vapor or Gas in Cells	Thermal Conductivity of Foam at 77°F $(Btu/(hr)(ft^2)(\ F/in))$	
	Experimentally Determined (where data are available)	Calculated From Table V- Using Eqs. (1) and (2)
A. Pure Gases in Cells		
Air	0.227	0.2234
CO_2	0.170-0.185	0.1600
Iso-Pentane	-	0.1443
B. Pure Halocarbons in Cells		
F-11	0.110-0.126	0.1022
F-12	-	0.1117
Methylene Chloride	-	0.1001
Chloroform	-	0.0978
Methyl Chloride	-	0.1193
C. Mixed Gases in Cells[a/] (Vapor 60.4% halocarbon)		
F-11	0.127	0.1255
F-112	-	0.1313
Chloroform	-	0.1228

[a/] Average analysis of gases in 24-hr foams: 7.3% air; 30.3% CO_2; 60.4% F-11; 2% unknown (see Table V-7 for details).

TABLE V-7

CELLULAR GAS ANALYSIS FROM RIGID URETHANE BUN STOCK[a,14]

Sample No.	Cell Gas Composition (mol %) Air	CO_2	CCl_3F	Unknown (H_2O?)	K Value of Foam[b]
1	8	34	57	2	0.12
2	9	27	61	2	0.13
3	6	31	61	2	0.12
4	7	32	59	2	0.12
5	6	30	62	2	0.12
6	8	28	62	2	0.12
Average	7.3	30.3	60.3	2.0	0.127

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a/ All foams identical formulation, prepared on bun machine. Density of all samples is 2.0716 lb/ft^3, except No. 4, which was 1.7716 lb/ft^3.

b/ Determined by garded hot plate method.

TABLE V-8

FLEXIBLE URETHANE FOAM CONSUMPTION (million pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975 (P)	1980 Est.	Growth Rate 1980/1973
Total reported by trade	255	307	356	480	528	635.5	673	724.9	954.8	998.8	1,014	1,690	8.5%
Bedding					58.8	78.0	83.4	93.5	114.4	132.6	136.4	175	6.2%
Furniture					195.0	207.5	220.0	239.8	369.6	365.0	352.0	670	8.9%
Packaging					14.0	13.0	11.0	15.1	16.5	17.6	19.8	50	17.0%
Textile laminates (except carpet)					16.0	20.5	26.5	39.6	31.9	33.4	26.4	60	9.5%
Transportation					179.0	225.0	257.4	288.2	363.0	374.0	341.0	440	3.0%
Other					29.7*	59.8*	22.1	24.6	25.4	26.6	17.6	50	10.0%
Rug underlay:													
Prime					18.0	23	21.8	28.6	31.9	32.3	30.8	110	19.0%
(recycled[a])					(25)	(27)	(36)	(50 est.)	(60)	(NA)	(NA)	(250)	
Total flexible foam (prime)					511.1	626.8	643.0	729.0	952.7	981.5	924.0	1,555	7.3%
Total all flexible urethane foam					536.1	653.8	679.0	779.0	1,012.7	-	-	1,805	8.6%

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[a] Prompt scrap and reclaimed foam shredded and rebonded to form controlled density, resiliant padding.

* Note: Other applications reallocated starting in 1971; cushioned rotovinyl flooring, recreational cushioning, special pads and cushions, etc.

Source: Compiled by Midwest Research Institute from 17 recent trade reports and forecasts.

* Almost all flexible urethanes are produced in plants; on-site foaming is rare.

* Large production runs are made of specifically engineered products and shapes.

* Mechanical properties and dynamic behavior of flexible foams are much more important.

* A wide range of foam densities and stiffness (resilience) is produced.

* Product specifications are tighter, requiring much greater use of instrumentation and automation.

* Virtually no equivalent of froth foaming process is used.

* Interconnecting, open-cell structures are predominately produced.

Of special importance for flexible foams used in automotive seating, furniture cushioning and textile applications are specifications and testing for:

* Foam density;
* Cell structure;
* Indentation load deflection;
* Compression set;
* Tear resistance;
* Elongation;
* Tensile strength;
* Flexural fatigue;
* Chemical and solvent resistance;
* Aging and oxidation resistance;
* Flammability;
* Resilience (falling ball, or pendulum); and
* Humidity aging.

The emphasis placed on achieving uniformity and predictable properties in flexible slab stock or molded foams makes the formulation and processing of flexible foams more critical than is the usual case for rigid foam. Any changes in foam blowing technology would have to be thoroughly tested and proven before being generally adopted.

c. Blowing agents for flexible urethane foams: All commercial flexible urethane foam systems employ as the principal blowing agent, carbon dioxide which is generated by the reaction of water with free isocyanate groups. The amount of water in the formulation will determine the density, and to a lesser extent the hardness of the foam.

While the density of flexible foams can be lowered simply by increasing the isocyanate and water levels, the range of control is limited because excess water changes the polymer structure of the foam. Therefore, auxiliary blowing agents are widely used to obtain lower foam density. Formulations typical of both CO_2 blown and fluorocarbon assisted flexible foams of different types are given in Table V-9. The level of FC blowing agent ranges from 3.6 to 12.5% for most flexible systems, substantially lower than blowing agents in rigid foams.

The use of volatile solvents to augment CO_2 blowing permits foams to be produced at lower cost, and with both improved properties and superior aesthetic qualities. When foams are blown with CO_2 alone, higher proportions of the most expensive main ingredient--the isocyanate--must be used simply to provide the CO_2 for foaming. Fluorocarbons and other volatile solvents permit conserving use of isocyanates. There has been a continuing shortage of aniline capacity in the U.S. which has kept certain isocyanates in short supply. Given these economic considerations, foam producers have strong incentives to utilize fluorocarbon assisted foaming systems.

Possibly of even greater importance is the control over foam softness and compression that is provided by the use of fluorocarbon blowing agents. Concentrations of 2 to 6% of F-11 in the formulation produce a considerable amount of softening. The density and load-bearing capacity of a given formulation can be varied, within limits, by merely increasing or decreasing the amount of fluorocarbon that is introduced at the mixing head.

Increasing the amount of fluorocarbon in a conventional one-shot formulation results in a decrease in both density and load-bearing properties. If high concentrations of fluorocarbon are used, both the catalyst concentration and the silicone stabilizer level must be increased in order to efficiently trap the large volume of gas which is generated.

Fluorocarbon-auxiliary-blown foams are always softer than foams of the same density which are blown only with the carbon dioxide generated by the isocyanate-water reaction. This difference in modulus occurs because the CO_2-blown foam has a greater crosslink density and thereby, a stiffer polymer chain in the foam structure.

Fluorocarbons also provide a desirable cooling action during foaming, which has an important effect on the state of cure. Adding F-11 to the foam formulation reduces the extent of heat buildup,

TABLE V-9

TYPICAL FORMULATIONS FOR FLEXIBLE URETHANE FOAMS

	FC Blown Polyether Slab a/	FC Blown Polyether Slab b/	CO_2 + FC Blown Polyether Slab c/	CO_2 Blown High Load Bearing a/	C Blown High Load Bearing a/	Extra-Supersoft Foam a/
Polyol	105.0	100.0	100.0	100.0	100.0	100.0
Isocyanate	43.7	46.0	54.3	64.9	51.0	34.1
Tin Catalyst	0.4	0.4	0.3	0.4	1.0	0.2
Amine Catalyst	0.3	0.2	0.1	0.1	-	0.2
Surfactant	2.0	1.0	1.0	1.2	1.2	3.0
Cell Opening Agent	-	-	-	5.0	5.0	-
Water	3.5	3.6	4.3	5.3	1.5	2.4
Fluorocarbon	0.0	6.4	6.0	-	10.0	20.0
Percent FC	0.0	4.0	3.6	0.0	5.8	12.5
Density, pcf	1.6	1.4	1.21	1.2	5.3	1.25
Tensile, psi	21.0	14.0	16.6	15.3	21.2	6.2
Elongation, %	430	220	192	150	101	149
Tear, lb/in.	4.0	2.2	2.7	5.4	1.8	1.2
Compression Set						
50% Deflection	-	6	-	-	1.6	10.3
90% Deflection	10	5	4.9	-	-	-
Indentation Load Deflection						
25% Deflection	36	30	34	40	79	9
65% Deflection	66	57	62	55	170	20.4
Ratio ILD 65%/25%	1.8	1.9	1.8	1.4	2.2	-
Rebound Falling Ball, %	40	38	-	-	10	-
Hepteresis Return, %	-	-	66	37	70	-

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a/ Frisch and Saunders (1972).
b/ Benning (1969).
c/ Dow (1974).

as illustrated in Table V-10. As the concentration of this fluorocarbon increases, the maximum temperature in the slab decreases, and the time to reach maximum temperature increases. The heat capacity and vaporization of the fluorocarbon undoubtedly are contributing factors to the reduction of the exotherm. Formulations containing high levels of fluorotrichloromethane may yield foams with higher than normal compression set. Such foams are usually given additional postcures at 250 to 275°F for 1 hr or more extended postcures at room temperature.

The use of a fluorocarbon as an auxiliary blowing agent in one-shot foams also serves to increase the 65:25 percentage indent load deflection (ILD) ratios. Specifications based on 65:25 ILD ratios greater than 2.0 have been instituted for most automotive cushioning.

The importance of the "feel" of flexible foams must be recognized. The dynamic behavior of cushioning used for bed pillows, chair seats, mattress toppers and, especially in clothing as fabric/foam laminates, is exceedingly critical. The earliest attempts to use flexible foams in garments were not successful largely because users judged the foam layers to be too harsh, lacking in drape, with low resilience and high hysteresis. Within the past 10 years, considerable improvement has been achieved in the production of softer foams having better tactile and mechanical properties.

A wide range of foam softness classes is produced today. The normal means of classifying flexible foams is according to the load required under standard test conditions (called the Indent Load Deflection; ILD-25%).

	ILD Range at 25% (lb)
Extra Firm	44 ± 6
Firm	34 ± 4
Medium	27 ± 3
Soft	21 ± 3
Super Soft	15 ± 3
Extra Super Soft	9 ± 3

Since about 1970, some manufacturers have introduced even softer grades sometimes called "Hyper Soft." The ILD-25% does not adequately characterize the differences between these special low hysteresis foams and the normal range of soft foams. Either the ILD at 10%, or the ratio of ILD at 65%:25% gives a better measure of the properties of Hyper Soft foams.

TABLE V-10[24]

COOLING EFFECT OF FLUOROCARBON-11 IN RESILIENT FOAM SLABS

$CFCl_3$ in Foam Formulation (parts/100 parts resin)	Maximum Exotherm Temperature in Slab[a] (°F)	Time to Reach Maximum Exotherm Temperature (sec)
0	224	200
2.5	223	260
5.0	215.5	300
7.5	210.5	300

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[a] Starting temperature of foam intermediates was 75°F.

The use of fluorocarbon blowing agents has been essential in achieving extreme softness and low hysteresis. Table V-11 compares the properties of CO_2 (water) blown soft foams and those utilizing high proportions of F-11 as the blowing agent. At present, no other blowing agent is known that can provide the desired properties for soft, low hysteresis foams in the super soft range and softer (i.e., ILD-25% below 14 lb).

TABLE V-11

PROPERTIES OF SOFT FLEXIBLE FOAMS

A. Blown Without Fluorocarbons

Density (lb/ft^3)	1.6	1.5	1.5
ILD-25% (lb)	14	16	20
ILD-65% (lb)	26	30	36
ILD Ratio 65:25%	1.85	1.88	1.80

B. Blown With 20% F-11

Density (lb/ft^3)	1.0	1.0	1.0
ILD-25% (lb)	5	6	7
ILD-65% (lb)	11	12	14
ILD Raio 65:25%	2.2	2.0	2.0

d. Other auxiliary blowing agents: Methylene chloride is the only auxiliary blowing agent other than the fluorocarbons which has been widely used commercially.[25] Because of its lower molecular weight, methylene chloride furnishes a slightly greater volume of vapor per unit weight. Its higher boiling point and higher polarity cause methylene chloride to remain dissolved in the foam at the end of the rise. A special inhibited grade of methylene chloride is offered as a blowing agent for flexible urethane foams.[23] In both slab stock and molded foams, it is claimed that the inhibitor minimizes deterioration of the foam by oxidation and subsequent scorching, producing a nonyellowing foam.[26] Methylene chloride is also the solvent generally used to wash out urethane production machinery for cleanup.

C. Polystyrene Foams

Four commercially important classes of styrene foams are widely produced in the United States. These include:

1. Extruded boardstock (Styrofoam®);
2. Expandable bead foam products;
3. Extruded foam sheet and film; and
4. Molded (high density) structural foams.

The first three types of foams utilize some form of volatile organic vapor as the foam blowing agent. The relatively high density, structural foams (used for bottle carriers, industrial pallets, furniture and machine parts, etc.) do not use volatile solvents, but typically rely on thermally unstable organic blowing agents. These structural foams will not be considered here. The technologies used in blowing the first three types of styrene foams will be discussed briefly, with emphasis on the use of volatile blowing agents.

1. Extruded boardstock: The first commerical polystyrene foam was extruded expanded board, developed by Dow during World War II. Molten polystyrene containxng methyl chloride as the blowing agent is extruded to form large foam logs, which are then cut into the desired standard board shapes. Major uses include building construction, cold storage insulation, and the floral trade.

Equipment for extruding expanded styrene board using volatile or gaseous solvents to generate the foam comprises (a) a holding chamber, (b) a mixing conveyor discharging through an orifice into (c) a tunnel within which the foam expands and is shaped. Because flammability is so important in the construction field, foams containing flame retardants (such as acetylene tetrabromide) are widely produced. These foams generally incorporate blue pigments which serve as nuclei for vapor formation and also identify the self-extinguishing grades.[27]

Several systems have been demonstrated that can generate styrene foams on-site for building construction, tank insulation and other applications. To date this type of foam production in the field has not been widely used.

Typical styrene boardstock has a density of 1.7 to 2.0 lb/ft^3. Nearly 40 million pounds of expanded styrene board were produced in 1974. The foam is relatively brittle, which is an advantage for florists because flower stems can be forced into the green foam supports. Closed cell structure and low water permeability make styrene logs suitable for dock flotation and other marine uses.

For critical insulating applications, a special "low K-factor" grade of foam was developed. This foam contains fluorocarbon vapor from the blowing agent trapped within the cells, effectively reducing the thermal conductivity of the insulation foam.

The incorporation of some F-12 along with methyl chloride reduces the tendency of freshly prepared foams to warp.[28] To achieve stable, low warpage foams, sufficient fluorocarbon is added so that diffusion of blowing agent vapor out of the foam is several times higher than the rate of diffusion of air into the foam. In some cases, the use of normally liquid blowing agents such as methylene chloride, benzene or acetone has been practiced instead of the more common use of methyl chloride and low boiling point fluorocarbons.[29]

Extruded styrene logs and board represent only a minor usage of fluorocarbon blowing agents compared with other types of styrene foams, or with urethanes. Less than 3 million pounds of extruded boardstock is blown in part with F-12, and these products typically use roughly 5 lb of fluorocarbon per 100 lb of foam.

2. Expandable bead foam products: The styrene foams produced in the greatest volume are generated by expanding and molding small styrene beads. In 1974, over 215 million pounds of bead foam was produced. The styrene bead cup for hot drinks typifies these molded items.

Styrene beads are generally expanded using hydrocarbon blowing agents such as the pentanes. Only a minor quantity of bead foams are blown using fluorocarbon agents. Total consumption of fluorocarbons is bead molding is estimated to be about 0.5 million pounds per year, which represents 10% of the fluorocarbons used in styrene foams.

Expandable styrene beads were first introduced about 1954, and volume production began after 1959. Billets of "bead board" for insulation was one of the first major products, although molded products, drink cups, and packaging applications now claim over 70% of production. The trade generally recognizes three size ranges of expandable beads. The smallest size designated as "cup beads," slightly larger beads called "molder's beads," and the largest sieve size range known as "board beads."

Bead foam products are molded from prepared beads of polystyrene which incorporate about 5 to 7% of volatile solvent. Blowing agent may be incorporated into the beads by a variety of methods, and the volatile agent is retained by the styrene polymer until expanded by heat. In fabrication, beads are usually pre-expanded (using either one-step pre-expansion, or multistage pre-expansion) with steam. As a separate step, the "pre-puff" is then charged into a mold where steam is injected causing further expansion as the beads fuse together in the desired shape. After a brief cooling step the molded part is ejected.

Pentanes are the agents most widely used for bead blowing, at a typical level of 6.3 to 7.0% by weight, although butanes, hexanes and other hydrocarbons are sometimes used to a minor extent. Nucleating agents such as sodium bicarbonate plus citric acid are mixed into the beads to initiate bubble formation by the volatile solvent. Foam formation is quite sensitive to the quantity of blowing agent used, and an excess of about 1% is sufficient to cause collapse of most foams. Neo-pentane, boiling at 9.5°C produces exceedingly fine cells, and is normally used only for specialty products, or in mixtures with other blowing agents. Iso-pentane, boiling at 28°C, gives small, uniform cells, and is the agent generally preferred for producing the lowest density foams. Iso-pentane, despite its lower boiling point and higher vapor pressure, is retained within the beads better than normal pentane. For most bead foams, normal pentane, boiling at 38°C, is used as the primary blowing agent.

Occasionally fluorocarbons are employed for special purposes. The use of F-11 and F-12 has become fairly well established since 1967 for blowing foams of lower density; for insulating foams; and in flame resistant products. In certain types of suspension polymerized beads, F-114, boiling at 3.8°C, is incorporated just as the polymer reaches the bead forming stage.[30,31/] Sometimes a mixture of 10% methylene chloride plus 90% pentane is used to blow the foam.

Providing that fluorocarbons are properly incorporated into the beads, they are retained as long as pentane, because they are less soluble in the styrene polymer, and permeation out of the bead or foam is thus retarded. However, the higher cost of fluorocarbons, together with the smaller volume of vapor produced per unit weight of blowing agent restricts their use to a small quantity of the bead foam produced, primarily in applications where fire hazards are a major consideration.

3. Extruded foam sheet and film: By far the largest use of fluorocarbon blowing agents in styrene foams is for production of foam sheet or film from crystal polystyrene. First introduced in the mid 1960's, consumption of foamed extruded sheet grew to about 70 million pounds by 1969. By 1974, use more than doubled, exceeding 200 million pounds. Egg cartons and foamed meat trays are typical of this class of styrene foams. A high molecular weight, crystal polystyrene is the starting material, so that these styrene foams are often referred to as "foamed from crystal."

Foamed sheet and film are produced by a single step extrusion process. Crystal resin is melted in the extrusion machine; blowing agent under pressure is introduced into the mixing zone of the barrel; and the resin mixture is extruded through a circular die as it expands forming a cylinder. The foam is pulled over a sizing mandrel, slit and wound as a flat sheet. Thicknesses typically range from 0.050 in. up to 0.125 in. or more. The sheet or film is then postheated and can be vacuum formed or pressed into the final shape.

In smooth or textured sheets, as well as molded forms, this extruded foam competes with a variety of paper and molded paper pulp products. Food packaging, disposable plates and other servicewares, decorative ribbons, and waffle-textured sheets used to protect furniture in shipment are growing applications. The foam sleeve jacketing recently introduced for soft drink bottles has been a notable development for the glass container industry.

Either pentanes or fluorocarbons can be used in extruding styrene foams from crystal. Blowing agent levels are typically 6.0%, which is similar to the proportion used for bead foams. While pentanes are used for more than 60% of all extruded sheet foams, the use of fluorocarbons, especially F-11 and F-12, has become more common since about 1967. Use of fluorocarbons permits the production of products of lighter weight and desirable tactile properties of drape and "feel." Mixtures of pentane and the fluorocarbons are sometimes used. One commercial process for foamed polystyrene sheet utilizes a 4:1 mixture of propane and tetrachloroethylene, plus the customary mixture of sodium bicarbonate and citric acid as the nucleating agents.[32/]

Extruded polystyrene sheet foamed from crystal is estimated to consume from 6 to 10 million pounds of fluorocarbons per year. After a year or two, practically all fluorocarbon has been lost from polystyrene foam, regardless of type.

D. Olefin Foams

In the early 1950's, plastic foams based on polyethylene and other polyolefins were first introduced. The original use, and still the largest volume application was as foamed medium density polyethylene foams for electric cable insulation (i.e., television lead-in and multi conductor telephone cables). The dielectric constant of the insulation layer is markedly improved by foaming the olefin polymer because of the contribution of the gas within the closed cells. For cable insulation, the polymer is expanded only about 100% using organic blowing agents (Celogen OT, Kempore, Unicel NDX, etc.). In 1973, over 25 million pounds of polyolefin was foamed for cable insulation, more than was consumed in all other olefin foams.

There are many processes for foaming olefins using organic pneumatogens that release nitrogen, CO_2 or other gases. Neither the organic blown foams, nor high density structural foams will be considered.

Polyethylene and other olefins are also fabricated by extrusion into foam planks, rounds, tubes and sheets. About 13 million pounds of these olefin foams were produced in 1973, over half of this quantity was fluorocarbon blown. The most successful process for expanding low density polyethylene foams is based on the use of fluorocarbon blowing agents.[33,34] The Dow Chemical Company's Ethafoam - a low density (2 lb/ft^3), closed cell foam having cells ranging from 0.5 to 1.0 mm in size, is typical of this class of foams.

Olefin foams are produced by forming a gel consisting of heat plasticized polyethylene having a high activation energy of flow and a volatile agent under pressure, and extruding the composition so as to obtain a controlled foam expansion. The most widely used blowing agents are F-114, F-12, and F-22.[35,36] Formerly, special purpose polyethylene and polypropylene foams were produced using perfluorocyclobutane (FC-318) as the blowing agent.[37] The foaming agent is fed into the mixing section of the screw, and on extrusion to the atmospheric pressure or reduced pressure evaporation spontaneously cools the viscous mixture to form a stable polyolefin foam. Most of the blowing agent diffuses out of low density olefin foams soon after formation.

E. Other Plastic Foams

Among the miscellaneous plastic foams that may employ fluorocarbons as blowing agent, are epoxy foams,[38] pyranyl foam,[39] vinyl plastisol foams,[40] and some phenolic and urea foams. It is likely that the fluorocarbons have been tried as blowing agents for nearly every kind of plastic and elastomer. The total quantity of such specialty foams is not reported, but annual production probably does not exceed 2 million pounds. Fluorocarbon usage is undoubtedly less than 0.2 million pounds.

F. Aggregate Consumption of Fluorocarbon Foam Blowing Agents

There are no official data on the quantities of fluorocarbons used in plastic foams, but various estimates have been published. Several of the recent estimates will be compared, and then revised estimates for each major type of foam will be presented.

Chemical Marketing Reporter has published estimates for fluorocarbon consumption by end-use distribution three times over the past 12 years, expressed as percentage of total FC production. When combined with production data, consumption would be:

Year	FC Used as Blowing Agents (% of Total)	Total Fluorocarbons U.S. Production[a] (million lb)	FC Used as Foam Blowing (million lb)
1963	5	423	21.2
1968	4	661	26.4
1973	7	1,056	73.9

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[a] Shamel, R. E., et al., "Preliminary Economic Impact of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons," Arthur D. Little, Inc., Contract No. 68-02-1349, Task 8, for Office of Air Quality, U.S. Environmental Protection Agency, Table II-1, p. II-3, September 1975; similar data from Tariff Commission source omits some fluorocarbons and results in somewhat lower production totals.

The IMOS Report[41] has compiled several estimates of fluorocarbon consumption by end uses. Based on data from U.S. Tariff Commission Reports, plus information from Stanford Research Institute and Du Pont, plastic foaming agent consumption for 1972 was placed at 50 million pounds of F-11 and 45 million pounds of F-12. This total of 95 million pounds represents 10.6% of the 889.6 million pounds of production estimated for 1972. One producer has indicated that actual use of F-12 in foams is substantially less than the 45 million pounds estimated for the IMOS Report.

The recent Arthur D. Little Report includes a table for usage of halocarbons in plastic foams for 1973 (reproduced here as Table V-12). The total of 90.2 million pounds was rounded down to indicate aggregate use of 88 million pounds of halocarbons which includes unspecified quantities of methylene chloride and methyl chloride.

A knowledgeable industry source[43] provided estimates for 1973 and 1974 blowing agent consumption as follows:

1. F-11 constitutes 80% of all fluorocarbons used in plastic foams during 1974. Foam blowing consumed nearly 25% of the F-11 produced in the United States.*

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* Note: Subsequent industry discussion leads MRI to believe that F-11 constitutes 70 to 75% of blowing agents, and that foams use only 15 to 17% of the F-11 production.

TABLE V-12

ESTIMATED U.S. USE OF HALOCARBONS IN PLASTIC FOAM MANUFACTURE - 1973[42] (million lb)

Type of Plastic Foam	Halocarbons Primarily Used	(1) Total Quantity of Foam Produced	(2) Estimated % Using Halocarbons	(3) Weight of Foam Using Halocarbon Blowing Agent	(4) Percent of Halo-Carbon Commonly Used in Formulation	(5) Quantity of Halocarbon Used	(6) Estimated % of Halocarbon Lost to the Atmosphere	(7) Estimated Quantity of Halocarbon Lost to Atmosphere[a]
Rigid polyurethane	F-11,12 frothing	350	85	300	15	44.8	20	9.0
Flexible polyurethane	F-11,113 mixture methylene chloride[b]	960	55	530	7	35.4	95	32.9
Extruded polystyrene sheet	F-12, F-11, pentane	140	50	70	7	4.9	95	4.7
Expanded polystyrene (EPS)	F-12 pentane	190	5	10	6	0.5	90	0.4
Extruded polystyrene board	Methyl chloride fluorocarbon	35	100	35	10	3.5	100	3.5
Polyolefin	F-114,12	11	65	7	16	1.1	95	1.1
Total		1,686	-	952	-	88 (adds to 90.2)	-	51

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[a] Although almost all of these emissions occur immediately, figure given is for emissions within 10 years.

[b] Methylene chloride used both as blowing agent and as solvent.

Source: Mod. Plast., January 1975, and Arthur D. Little, Inc., estimates.

2. For 1973, plastic foams consumed F-11 plus F-12 at levels of:

19	million lb flexible polyurethane foams
37	million lb rigid polyurethanes
7	million lb all other plastic foams
63	million lb F-11 and F-12 for blowing agents

3. In 1973, blowing agent use can be allocated as:

Agent	Million Lb
F-11	53
F-12	10
F-113	Small (< 2)
F-114	Small (< 3)
Total	< 73

To compare with previous estimates, MRI developed the figures given in Table V-13 for 1973 and 1974 usage of chlorofluorocarbons for plastic foams. Changes between 1973 and 1974 were not particularly significant. The level of blowing agent used in those flexible and rigid urethanes that employ fluorocarbons increased slightly due to greater production of frothed foam and soft flexibles, but this was partially offset by a corresponding rise in water blown urethanes. Somewhat higher consumption of FC in polystyrene sheet foamed from crystal was experienced in 1974. Total fluorocarbon use in all plastic foams for both years is believed to be close to 78 million pounds. Of this total, about 55 to 59 million pounds (roughly 70%) was F-11, while F-12 usage was between 12 and 14 million pounds. Estimates for other fluorocarbons used in smaller quantities are subject to large uncertainties, but probably does not exceed 6 to 7 million pounds.

G. Fluorocarbon Emissions from Foams

Blowing agents are trapped and retained within rigid urethane and epoxy foams for relatively long times. In contrast, blowing agents diffuse out of the foam structure very rapidly from flexible foams and more slowly from the nonpolar polymers such as polystyrene and polyethylene. In addition, the foam production processes entail varying losses of blowing agent during fabrication. Thus the quantity of blowing agent lost to the atmosphere during manufacture, subsequent use, and ultimate

TABLE V-13

FLUOROCARBON USAGE IN PLASTIC FOAMS 1973 AND 1974

Type of Foam	Foam Used (Million Pounds)	Percent Using FC	Lb FC (avg.)/ 100 lb Foam	FC Used (Million Pounds)	
1973					
Urethanes					
Flexible	952.7	50	5.0	23.8	
Rigid	362.4	86	14.0	43.6	
					67.4
Styrenes					
Expanded beads	202.4	4	6.0	0.5	
Extruded board	37.4	5	5.0	0.1	
Extruded foamed sheet	145.2	45	6.5	4.2	
					4.8
Olefins and Others[a]	12.0	0.55	15.0	1.0	
Total Fluorocarbons for Plastic Foams					73.2
1974					
Urethanes					
Flexible	998.8	45	5.0	22.5	
Rigid	374.0	88	14.5	47.7	
					70.2
Styrenes					
Expanded beads	217.8	4	6.0	0.8	
Extruded board	39.6	5	5.0	0.1	
Extruded foamed sheet	200.2	48	6.5	6.2	
					7.0
Olefins and Others[a]	13.5	60	15.0	1.2	
Total Fluorocarbons for Plastic Foams					78.4

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[a] Other foams include: Phenolic, Urea, Expoy, Polyester, Polyisocyanurate, Pyranyl, and PVC Plastisol foams.

disposal of plastic foams varies greatly. Among the factors that influence losses and emissions of fluorocarbons to the atmosphere are:

- Type of plastic foam.
- Density and structure of the foam.
- Percentage of open and closed cells.
- Solubility and diffusivity of blowing agent in the polymer.
- Surface area to volume ratio of finished foams.
- Enclosure or surfacing of foam with impermeable skins.
- Lifetime of foam in use, and ultimate disposal.

It has been confirmed that fluorocarbns are retained in rigid urethane, both by chemical analyses,[44,45] and by thermal measurements over long periods, as illustrated in Figure V-6.[46] Fluorocarbon losses during foam manufacture depend on the equipment used, and on whether a poured on frothed foam is employed.

Urethane foam plants must work with the relatively toxic isocyanates. Because the maximum permissible threshold limit values (TLV's) for isocyanates, are so low,* all plants are well ventilated and the foam production equipment is usually hooded to protect the workers. Fluorocarbon-11 concentrations, monitored in the breathing air near various stages of foam manufacture are shown in Table V-14.[47] These levels of fluorocarbon vapor are well below the allowable industrial exposures for fluorocarbons (TLV = 1,000 ppm).

In considering the quantities of fluorocarbons emitted to the atmosphere from plastic foams, the retention properties of rigid and enclosed foams must be taken into account. Despite the lack of data on such emissions, it can be shown that the retention and slow release over a period of years is not trivial, but reduces losses by perhaps 40%.

A recent estimate placed FC losses from all rigid urethane foams over a 10-year period at 20%[42] (see Table V-12). MRI estimates that 15 to 20% of the blowing agent is lost within days of production, and that an additional 10% diffuses out over the life of the foam. To simplify estimation, this 10% loss of blowing agent was allocated to the 5th year after foam production. If the fluorocarbons from all other foams are assumed to be lost to the atmosphere immediately or shortly after foaming, the expected emission pattern would be that shown in Table V-15.

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* TLV ceiling for TDI is 0.02 ppm, ANSI Z 37.36 (1973).

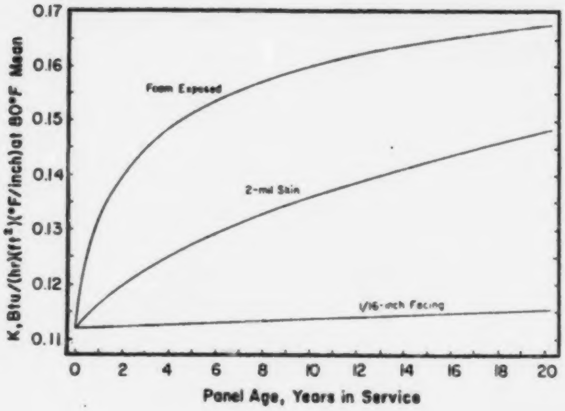

Figure V-6 - Conductivities of 1.8 In. Thick Cooler Panel Cores: Diffusion Through the 40°F Face

TABLE V-14

FLUOROCARBON-11 CONCENTRATIONS IN BREATHING ZONE AIR FOAM MANUFACTURING FACILITIES

	FC-11, ppm v/v[a]			
	Flexible Foam			
			Normal Production Rate	
Location	Rigid Foam Panel Production	High Production Rate Regular	Regular Foam	Supersoft Foam
Mix tanks	NA	NA	NA	NA
Foam head	113	178	62	88
Expansion - Begin	94	146	31	139
Middle	147	182	25	198
End	192	181	24	156
Cutting	64	181	15	130
Curing racks	NA	355	280	586
Product storage	12	NA	10	10
General building	70	61	26	47
Packaging/shipment	30	95	10	10
Laboratory/office	60	as general building		

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[a] All measurements from corrected POVA readings. Agreement with grab samples typically within ± 5%.

NA--Not available, e.g., no curing racks, tanks outside, etc.

TABLE V-15

FLUOROCARBONS IN FOAM--CONSUMPTION AND ATMOSPHERIC EMISSIONS

	Fluorocarbons (millions of pounds)			
	Used in Plastic Foams			
Year	Total All Foams	Rigid Urethane Only	Annual Emissions to Atmosphere[a]	Cumulative Emissions from 1965[b]
1965	11	7.7	5	5
1966	16	12.1	6	11
1967	19	14.0	8	19
1968	29	17.6	15	34
1969	35	22.4	18	52
1970	43	25.3	24	76
1971	46	26.7	26	102
1972	56	33.2	31	133
1973	73	43.6	40	173
1974	78	47.7	42	215
1975 (P)	77	48.8	41	256
Total	483	299	256	

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[a] Assuming 100% prompt emissions from foams other than rigid urethanes, plus 20% prompt emissions for rigid urethanes, with an additional 10% allocated to the 5th year after production.

[b] Use of FC-blowing agents negligible prior to 1960. Cumulative emissions from 1960 to 1964 are estimated to be less than 5 million pounds.

Source: MRI estimates based on Tables V-2, V-8, and V-13.
(P) = Preliminary

Although the numbers shown in Table V-15 are estimates, not based on well established data, they do illustrate a robust conclusion: atmospheric emissions are substantially less than fluorocarbon blowing agent usage. On either an annual basis, or cumulative since 1965 (fluorocarbon use prior to 1960 or 1961 was negligible), loss to the atmosphere is roughly one-half of total consumption of fluorocarbons in plastic foams.

The difference depends on two basic facts--(a) rigid foams use twice as much fluorocarbons as do flexible foam and other types of foams; and (b) a major portion of blowing agents used in rigid urethanes are retained for years. Eventually, on disposal of these foams, the retained fluorocarbons would presumably enter the atmosphere. Meanwhile, fluorocarbon losses to the environment are significantly less than total use in foams.

H. Alternatives to Use of Fluorocarbon Blowing Agents

If present uses of fluorocarbons in plastic foam fabrication were restricted, what technically feasible alternatives exist, or might be developed?

Several general possibilities should be considered:

1. Substitution of other materials for fluorocarbon blown foams.
2. Use of alternative blowing agents.
3. Modification of foam production technology.
4. Minimizing release of fluorocarbons to the atmosphere.

1. Substitute materials: Plastic foams have been introduced, largely since 1945, as preferred replacements for other materials. Either a return to former materials, or more likely, the introduction of new replacements for fluorocarbon blown foams is a distinct possibility.

Table V-16 presents a partial listing of current foam applications with some indication of possible substitutes for fluorocarbon blown foams. In many cases acceptable replacements are currently available. Certainly, there are important considerations such as practical fabrication, cost differences, or esthetic preferences that currently dictate the consumption patterns for plastic foams. Switching to alternative materials in the automotive seating, furniture and bedding, flotation, and packaging industries would cause problems. Consumers would certainly have to pay for changeover costs, and for more costly materials and fabrication.

TABLE V-16

POTENTIAL SUBSTITUTES FOR FLUOROCARBON BLOWN PLASTIC FOAMS

Current Foam Application	Substitute Materials[a]
Building insulation	Fiberglas®, urea foams, phenolic foams, Styrofoam®, perlite, vermiculite. (No satisfactory replacement for some uses.)
Refrigeration appliances	Pyranyl foam, Fiberglas®, microcellular silica, styrene foams. (No completely satisfactory equivalent.)
Industrial tanks	Foamglass, phenolic foams, syntactic foams, mineral wool blankets or spray. (No equivalent for low temperature applications.)
Pipe and pipelines	Fiberglas®, cellular rubber, phenolic foams, mineral fiber lagging.
Transportation carriers	Styrene foams, Fiberglas®. (No equivalent for subsequent insulation.)
Flotation and marine	Styrene foams, phenolic foams, olefin foams.
Packaging, molded shapes	Styrene foams, thermoformed sheet, molded paper pulp, blister pack and shrink film packaging.
Packaging, dunnage and cushioning	Olefin foams, styrene fill, sealed air bubble films, shaped corrugated board blocks, vermiculite, Excelsior, Shredded newsprint, creped paper.
Bedding	Innerspring mattresses, latex foams, Dacron Fiberfil, feathers and down.
Furniture and seating	Latex foams, rubberized hair, pocketed springs, zig-wire springs, elastomer cords, pneumatic cushioning.
Rug underlay	Hair-jute padding, rubber latex ripple underlay, sponge rubber.
Vinyl flooring, bonded foam	No general substitute.
Textile laminates	Quilted Fiberfil, Pellon, special knits. (No equivalent material.)
Flexible packaging foam	Latex foams, sealed air cap films, vinyl foams, rubberized hair.
Electric cable insulation	Radiation cross-linked olefin, neoprene inorganic insulations, pressurized gas insulation polybutenes.

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[a] Representative materials which could be substituted for the presently used foams. A few of the substitute foams such as pyranyl and olefin foams currently are FC blown; most of the other foams do not require the use of fluorocarbon-blowing agents.

There are in addition, several applications for which no acceptable or equivalent substitute is now known. Most critical of these are thermal insulation foams for construction--especially on-site application of rigid urethane foams. Other areas in which thermal properties depend critically on fluorocarbons include: refrigeration appliances and cold storage, industrial tanks for cryogenics or LNG, and application of thermal insulation to existing railroad cars and barge carriers.

While other plastic foams, notably the ureas and phenolic foams are available for on-site application as thermal insulation, they do not approach the K-factor provided by fluorocarbon vapors within the urethane foam cells. Foam thickness is restricted in thin building panels and curtain wall construction. Lower K-value foams would require up to double the thickness to provide equivalent insulation. Energy conservation efforts in residential, commercial and industrial buildings could be seriously hampered by the extra costs involved.

The fluorocarbon-blowing agents are not the only vapors capable of contributing low thermal conductivity to plastic foams. As discussed in Section B-2-d (pp. 99 to 105), other halogenated vapors also show low thermal conductivity (see Table V-4). Providing that these or similar compounds could be used in low density foams for thermal insulation, the K-factors theoretically obtainable should be acceptable. However, there are major practical problems that would have to be solved before satisfactory rigid plastic foams could be produced for thermal insulation without the use of the present fluorocarbons. (See discussion of requirements for any alternative blowing agent in Section H-2, pp. 131 to 137.) Although it may be possible in the future to develop a low K-value foam that does not require the use of fluorocarbon-blowing agents, there is no proven substitute presently available for use in insulation applications.

Refrigeration appliance manufacturers have stated that if fluorocarbon foamed urethane was not available, they would not choose to make wall cavities twice as thick and use CO_2-blown foams, but would probably return to fibrous insulation blankets. This would penalize the purchaser in terms of usable interior space, and in high energy cost of operation.

Large storage tanks such as those for liquid natural gas, not only depend on urethane insulation foams, but also on the froth spraying method of job-site application which uses additional fluorocarbon. Pipeline insulation applied in the field similarly depends on fluorocarbon expanded foam. Many railroads, now modernizing their rolling stock by insulation, have become dependent on spray applied foams for tank cars and hopper carriers.

Most flexible foams can be produced by CO_2 blowing. This increases foam cost by about 15% because of increased isocyanate consumption. Mechanical properties of water blown foams would suffer in several respects, but for most noncritical cushioning uses, nonfluorocarbon blown foams would be acceptable.

There is no known method of producing the super-soft flexible foams without using auxiliary fluorocarbon-blowing agents. Whether nonfluorocarbon agents can be developed for this purpose remains to be seen. Soft foams with low hysteresis and excellent recovery have become almost essential in automotive seating. So far as can be determined, it is not possible to produce highly resilient flexible foams of low density without the use of fluorocarbons.

Acceptable textile laminates having a soft hand and good garment draping characteristics are currently dependent on fluorocarbon blowing. To our knowledge, no suitable substitute blowing agent is available for this use.

Urethane rug padding, which has largely replaced latex foams and hair padding could be produced without fluorocarbons when made as a separate underlayment. However, many carpet manufacturers have developed integral or self-backed carpeting that uses resilient foam laminated directly to the backing. Producers were unable to speculate on the feasibility of making similar cushioned carpeting without the use of fluorocarbon expanded foams.

2. Use of alternative blowing agents: Foam-blowing agents must satisfy a variety of requirements. Lassman[48/] has listed the properties desired in a physical blowing agent such as the volatile solvents:

1. Agent should be odorless and nontoxic.

2. Agent should be noncorrosive.

3. Agent should be nonflammable.

4. Agent should not affect the physical and chemical properties of the polymer, although it may be soluble in, or swell, the polymer at low temperatures. Must not affect rate of polymerization or cure.

5. In gaseous form, the agent must be thermally stable and chemically inert.

6. Agent should possess a low vapor pressure at room temperature and thus lend itself to easy handling under ambient conditions.

7. Agent should have a fast evaporation rate (low specific heat and low latent heat of vaporation). Must vaporize over a definite temperature range.

8. Agent should have a low molecular weight.

9. Agent should have a high specific gravity.

10. In gaseous form, agent should possess a slower diffusion rate through the polymer membrane than air.

11. Agent should be readily available commercially.

12. For thermal insulating foams, vapor should have the lowest possible thermal conductivity.

It is unlikely that any volatile compound can satisfy all of the requirements for the ideal blowing agent. Moreover, the practical trade-offs among factors such as flammability, toxicity, latent heat of vaporization, vapor volume per unit of blowing agent, water solubility, etc., are not easily established. It is relatively difficult to predict in advance how the addition of any particular volatile agent will affect the foaming process, or exactly what the effect on foam properties will be. The established fluorocarbon agents have been proven over the years to be exceptionally satisfactory for both rigid and flexible urethane foams. It is logical that any alternative agent should approach the characteristics of these fluorocarbons as closely as practical in several key properties.

Remarkably little information on the suitability of nonfluorocarbon blowing auxiliaries has been published. In 1958 Klesper was among the first to report using volatile solvents for urethane foams.[49/] He tried acetone, ether and pentane, plus F-11 and other fluorocarbons. While all of the volatile agents did produce foams, acetone tended to soften the rigid urethane; pentane caused "a boiling action;" and ether had its characteristic odor and high flammability. The results obtained with F-11 were so superior that further investigations have been neglected.

Ten years later, Boucher and Murray made a study of 27 different solvents as blowing agents for a low-viscosity, highly exothermic rigid urethane foam system.[50/] They found that the times and temperature of such phenomena as cream, rise, cup, and gel are strongly influenced by the boiling point of the blowing agent as well as its chemical structure. Similar effects may be expected in flexible systems. Satisfactory foams were obtained with several of the higher boiling solvents, while many solvents produced faulty foams, or caused the foam to collapse. It is worth noting in this case that the particular foam system under study did not produce acceptable foams with F-11 or with methylene chloride or several other agents that are known to be satisfactory for the usual urethane foam systems. It is believed that the unusually high exotherm of the urethane reaction, and the effect of thermocouple probes was responsible for the poor results obtained with some solvents.

A few other solvents have been reported as blowing agents:

- 2-Chloropropane;
- Chloroform;
- 1,1,1 Trichloroethane; and
- Perfluorocyclobutane (FC-318).

The use of methylene chloride as a blowing agent in flexible foams is well established. Methylene chloride can be used as the sole auxiliary blowing agent, or it can be used in combination with F-11. Because of its lower molecular weight, methylene chloride produces more vapor per unit weight than does F-11, so that only two-thirds as much agent is required (see Table V-17). In many cases methylene chloride can be substituted directly in the reactive system without adjustment of proportions. Table V-17 compares the formulation and foam properties obtained using methylene chloride versus fluorocarbon-11. Foam density, ILD values, and other important properties of both foams were equivalent.

Blowing agent vapors exhibiting low thermal conductivity, and little tendency to diffuse out of the foam cells are essential for insulating foams. Some of the halogenated compounds listed in Table V-4 show relatively low K-values, and would be potential candidates for trial in rigid urethane foams. It may be possible to utilize blends or mixtures of several solvents to more nearly match the properties desired in various foam systems. Combination of ethyl chloride (b.p. 12.5°C), methylene chloride (b.p. 40.1°C) and 1-chloropropane have been suggested. In general, the volatility requirements limit blowing agents for polyurethane foams to materials boiling between 10 and 50°C.

Solvents other than the conventionally used fluorocarbon blowing agents are available to match almost any boiling point range desired (Table V-18). Some of the fluorocarbons listed are seldom used in foam production because of their higher cost. If these agents produce acceptable foams they might be suitable replacements for any fluorocarbon that is restricted. The cost of blowing agents used in foams is a small part of the cost of the finished foam but is still an important factor.

TABLE V-17

FOAM FORMULATIONS AND PROPERTIES[23]

Sample Formulations, PHP[a]	A[b]	B[c]
VORANOL Polyol 3010	100	100
Water	4.3	4.3
L-540 Silicone	1.0	1.0
NIAX A-1 Amine Catalyst	0.10	0.10
T-9 Stannous Octoate	.20-.30	.20-.30
Isocyanate Type: HYLENE TM/80/20 (TDI Index 108)	54.3	54.3
F-11	6.0	-
$MeCl_2$ U.G.	-	4.0
	165.9	163.9
Physical Properties	**Values**	**Averaged**
Density, lb/ft^3	1.21	1.27
Tensile, psi	16.6	16.5
Elongation, %	192	193
Tear, lb/in	2.7	2.9
Resiliency, % DB	47	47
Compression set 90%	4.9	4.3
4 in. ILD 25%	34	33
4 in. ILD 65%	62	61
% Hysteresis Return	66	66
Modulus	1.82	1.85
Air Flow, Middle	5.0	5.8
Processing Conditions		
Thruput, lb/min	150	
Polyol/TDI Temperature, °F	75/75	
Sitrrer RPM	4,800	
A.B.S. Humidity, g/lb	70	

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[a] Parts per hundred parts polyol.

[b] F-11 blowing agent.

[c] Methylene chloride blowing agent.

TABLE V-18

VOLATILE COMPOUNDS BOILING POINT -40 TO 100° C

Fluorocarbon No.	Compound	B.P. °C
	Propane	-42.1
22	$CHClF_2$	-40.8
115	C_2ClF_5	-38.7
	CH_3CH_2F	-37.1
	Cyclopropane	-32.9
12	CCl_2F_2	-29.8
	$CH_2F - CF_3$	-26.5
	Methyl Chloride	-24.1
	Dimethyl Ether	-24.1
	$CHBrF_2$	-15.0
	Isobutane	-11.7
	Methylamine	- 6.5
FC-318	Perfluorocyclobutane	- 5.9
	$CBrClF_2$	- 4.0
	Butane	- 0.5
114	$C_2Cl_2F_4$	3.8
	Methyl Bromide	4.6
	Vinyl Methyl Ether	5.0
133	CH_2ClCF_3	6.1
21	$CHCl_2F$	8.9
	Neopentane	9.5
	Ethylene Oxide	10.7
	Ethyl Methyl Ether	10.8
	Ethyl Chloride	12.5
	Cyclobutane	13.1
	Ethylamine	16.4
	1,1-Dimethylcyclopentane	20.6
	Perfluorocyclopentane	22.0
11	CCl_3F	23.8
	CBr_2F_2	24.5
	Isopentane	27.9
123	$CHCl_2CF_3$	28.2
	Methyl Formate	31.4
	Furan	31.6
	Diethyl Ether	34.6

TABLE V-18 (Concluded)

Fluorocarbon No.	Compound	B.P. °C
	n-Pentane	36.0
	Ethyl Bromide	38.0
	Methylene Chloride	40.1
	1-Chloropropane	46.4
	Carbon Disulfide	46.5
114B2	$C_2Br_2F_4$	47.3
113	$C_2Cl_3F_3$	47.6
	2,2-Dimethylbutane	49.7
	Perfluorocyclohexane	50.0
	Ethyl Formate	54.2
	Acetone	56.1
	Ethylene Dichloride	57.3
	Methyl Acetate	57.4
	2,3-Dimethylbutane	58.0
	Chloroform	61.0
	CH_2ClBr	68.5
	2,2-Dichloropropane	70.0
	1,1,1-Trichloroethane	74.1
	Benzene	80.1
	Cyclohexane	80.7
	Perfluorocycloheptane	82.5
	2-Methylhexane	90.1
112	$C_2Cl_4F_2$	92.8
	Methylene Bromide	98.2
	n-Heptane	98.4

The cost of all materials for foams similar to those of Table V-17 ranges from \$0.50 to \$0.60/ft^3 of foam. At current prices, the F-11 blowing agent represents about 4% of ingredient cost; or less than 2.5¢/ft^3. If comparable ammounts of some other blowing agent costing three times as much as F-11 were used, ingredient cost would be increased by about 5¢/ft^3, or nearly 10%. The cost of fabricated foam to the user would be increased by about half this percentage. If all 78 million pounds of fluorocarbons used in 1975 to produce foams were replaced by agents costing about \$1.20/lb (an additional \$0.80/lb), the increased cost would total \$62 million. For an annual output of 898 million pounds of fluorocarbon-blown foam, the added cost would amount to 6.5¢/lb.

3. Modification of foam production technology: For certain purposes it may be possible to produce plastic foams by means other than internal generation of vapors and gases. Some attempts have been made to mechanically whip polymer systems into a stable foam. The presence of dissolved air or gas in urethane foam reactants provides nucleation indispensable to foaming,[51] but efforts to use gases such as nitrogen, carbon dioxide, argon, or air as auxiliary blowing agents in slab production have not been commercially successful.

The Carborundum Company has developed a process for expanding urethane foams in a vacuum.[53] The properties of vacuum-blown foams are unusual and offer promise of wide applicability. These foams are blown in vacuum without any blowing agent; they are tougher, have a higher resistence, have better resilience, and lower compression set. However, these rigid foams have been used thus far only for special purposes.

At the present time, techniques for fabricating plastic foams without the use of either CO_2 or auxiliary blowing agents have not been developed to a practical technology. Since foams for thermal insulation depend upon the low conductivity of vapors within the cells, it is not likely that any new foam fabrication process would be suitable for preparing insulating foams.

4. Minimizing release of fluorocarbons: A certain amount of blowing agent is lost during any type of on-site foam application. Even where wall cavities are filled on-site, some release of volatile agent is unavoidable. Self-skinning foams as applied on tanks and roof decks help to prevent subsequent release to the atmosphere, as does the application of weatherproof coatings.

Foams produced under controlled conditions in plants offer the possibility of collecting and recovering most of the blowing agent released during fabrication. While all slab stack and bun foam machines are hooded, and vapors are removed through ventilating ducts, virtually no attempt has yet been made to recover volatile blowing agents because of the very high anticipated cost of recovery systems.

Because the vapors from foam production lines contain highly reactive and toxic isocyanates, and other organic compounds plus water vapor, many types of solvent recovery systems cannot be used. It would appear technically feasible to prescrub the vapors evolved during foam production, thus removing the contaminants that interfere with fluorocarbon recovery and leaving the chemically stable fluorocarbons sufficiently free of contaminants that collection and purification for reuse would be possible. Recovery of 90% of the fluorocarbons from flexible foams would collect about 20 million pounds per year, valued at $8 million. Much less fluorocarbon recovery would be possible from rigid foams; perhaps 5 to 6 million pounds per year could be collected from boardstock lines and curing rooms.

However, practical processes for vapor pretreatment, recovery, and purification of blowing agents remain to be developed. The equipment required would need to be corrosion resistant. Because process equipment for fluorocarbon recovery has not yet been developed, consideration of economics is premature. However, in certain cases where it has been necessary to install other vapor recovery systems to comply with regulations, the savings derived from recovery have largely justified the costs of the extra equipment and processing required.

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VI. CLEANING AND DRYING SOLVENTS

This section addresses the technical considerations for the use of alternative chemicals and/or mixtures in the areas of chlorofluorocarbon solvent cleaning and drying. This market can be broken down into five applications:

Defluxing and electronics cleaning;

Degreasing;

Displacement drying;

Dry cleaning; and

Miscellaneous specialty applications.

The current overall utilization in each application can be deemed minor with respect to both the total overall chlorofluorocarbon consumption and the consumption of other solvents in each of the applications under consideration. However, in many cases, the chlorofluorocarbons are either the solvent of choice based on value-in-use or the only solvent capable of providing the cleanliness levels required by military specifications.

From data presented in the A. D. Little report, various issues of the Chemical Marketing Reporter, and adjustments of these figures by personnel directly related to the cleaning and drying industry but not related to the actual manufacture of these products, the estimated 1975 consumption of F-11 (and F-112), and F-113 in the applications is very small (approximately 1/20 or 5%) when compared to the competitive chlorocarbons, as shown in the following tabulation.

Chemical	Fluorocarbons, Million Pounds	Chlorocarbons, Million Pounds
F-11 (and F-112)	5.5-6.0	
F-113	54-62	
1,1,1-Trichloroethane		360-390
Trichloroethylene		370-390
Perchloroethylene		515-575
Methylene Chloride		110-120
Total	59.5-68	1,355-1,475

From the discussions presented in the three previous sections on refrigeration and air conditioning, aerosol industry, and foam-blowing agents, it can be readily observed that the utilization of chlorofluorocarbons in these areas (~ 63 million pounds) constitutes a small percentage of the overall chlorofluorocarbon consumption (~ 9%).

In addition to their thermodynamic advantages of high vapor pressure and low boiling points, the chlorofluorocarbons F-11 and F-113 have very useful solvent properties, which make them suitable for the cleaning and drying industries. Alternative chemicals are available and widely used in both of these industries. However, the two chlorofluorocarbons afford the advantages of: nonflammability, high vapor pressure which results in rapid drying, low heat of vaporization, low order of toxicity, high density, low surface tension, chemical inertness, chemical stability to heat and materials, purity, and selected solvency as compared to many of the alternatives. In many instances, it is the specific combination of properties offered by the pure chlorofluorocarbons, blends, or azeotropes which make them an economically justifiable cleaning system. Although alternate chemicals (chlorocarbons) are available and widely used in these markets, compromises in employee health and safety, technical performance, energy utilization, and waste disposal often reduce their overall value-in-use.

In the subsequent subsections, the areas of solvent cleaning and drying will be discussed individually with respect to the technical considerations for utility, current status of the various chlorofluorocarbon solvents, and alternative systems for the two chlorofluorocarbons, F-11 and F-113.

A. Chlorofluorocarbons Used in Cleaning and Drying

The selection and evaluation of alternatives in the cleaning and drying industry is quite difficult to assess primarily because each problem, or cleaning and drying application, is unique in that a particular type of soil and/or grease must be removed from a specific item or piece of hardware which in turn is fabricated from a range of materials (metals, metal oxides, plastics, glass, elastomers, etc.). Consequently, degreasing solvents for a particular application often have been tailored to a specific problem. Thus identification of specific alternatives to F-11 and F-113 is very difficult in the absence of detailed knowledge concerning the specific degreasing problem.

1. General criteria for degreasers: There are basically three systems or methods for material cleaning and drying: (a) cold cleaning; (b) vapor degreasing; and (c) flushing. The first two of these methods may be supplemented by the use of ultrasonic equipment if deemed necessary for a specific application.

In very simplified terms, cold-cleaning systems consist of a container for the solvent and some mechanism to immerse and remove the material to be cleaned. The solvent remains basically at room temperature and the cleaning action, without ultrasonic equipment, is based entirely on the solubility properties of the solvent. A more detailed discussion of the mechanisms of cold-cleaning and vapor-degreasing systems has been given in the Arthur D. Little report[1/] so that any detailed discussion at this point would be redundant. The general criteria to be considered for cold-cleaning applications are as follows:

- Compatibility of the solvent with the material to be cleaned.
- Volatility.
- Stability.
- Cost of solvent.
- Toxicity.
- Flammability, although not as critical as for vapor degreasing.
- Solubility parameters.
- Recoverability.
- Solvent composition; azeotropes or nonblends are desirable to eliminate composition change.

Some properties of commonly used solvent materials are shown in Table VI-1.

For vapor degreasing, the solvent is heated to form a hot vapor zone above the liquid. The function of the vapor zone is two-fold. It serves as both a cleaning medium and a means of vapor emission control. In properly designed and properly applied vapor degreasing systems, solvent loss can be controlled quite effectively. In these systems, vapor density becomes an extremely important factor. The higher the vapor density the easier it would be to retain solvent vapors within the system.

Typically, vapor degreasers are of two basic types: those designed with only a boiling sump or vapor generating means and those containing a secondary rinse chamber as well. In a simple vapor degreasing operation, the part to be cleaned is immersed into the vapor zone where hot solvent vapor condenses on the cooler part. Soil and grease are removed from the part and are collected in the boiling chamber. Condensate collected in the condensing zone of the degreaser is first passed through a water separator where any moisture generated in the condensing process is separated from the condensed solvent. This water separator also functions as a source of distilled solvent in the event a distilled solvent spray is desired. Following separation of water, the solvent is returned to the boiling sump.

TABLE VI-1

PROPERTIES AND COSTS OF COMMONLY USED SOLVENT VAPOR DEGREASING MATERIALS[a]

	Flash Point (°F)	OSHA TWA (ppm)[b]	Boiling Point (°F)	Latent Heat (Btu/lb)	Specific Heat (Btu/lb/°F)	Vapor Density (Air = 1)	Solvency (KB Value)	Stability in Presence of H_2O[c]	Restrictions	Cost Per Gallon[d] ($/Gal.)
Methylene Chloride	None	500	102-106	141	0.28	2.96	136	c/	e/	1.95-1.98
Perchloroethylene	None	100	250-254	90	0.21	5.71	90	c/	-	2.22-2.26
Trichloroethane (1,1,1)	None	350	162-190	102	0.25	4.55	124	76.7	f/	2.12-2.14
Trichloroethylene	None	100	188-190	103	0.23	4.53	130	9.0	g/	2.155-2.195
Trichlorotrifluoroethane (F-113)	None	100	117.6	63	0.22	6.47	31	Nil.	-	6.53

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a/ Data supplied by a major producer of chlorofluorocarbons.

b/ OSHA - 8-hr time weighted average expressed in parts per million of solvent vapor.

c/ Tests run using 200 ml of solvent containing 0.1 g of iron powder and refluxing through a water separator in a modified Soxhlet extractor for 100 hr. At the end of the test, the increase in the test system (HCl equivalent) was determined. Methylene chloride and perchloroethylene were not run, but methylene chloride is considered to be* "Fairly stable in the presence of water," and perchloroethylene to be the "least susceptible" of the chlorinated solvents. * Selecting Alternative Chlorinated Solvents, Archer - Metal Progress, p. 133, October 1974.

d/ Chemical Marketing Reporter.

e/ There is some concern developing regarding the elevation of carboxyhemoglobin following exposure to methylene chloride. Refs. Carboxyhemoglobin Elevation After Exposure to Dichloromethane - Stewart, Terrance, Fisher et al., Science, 176, 295 (1972). Experimental Human Exposure to Methylene Chloride - Stewart, Terrance, Fisher et al., Archives of Environmental Health, 25, 342 (1972).

f/ Dioxane, an inhibiting agent commonly used in trichloroethane, is listed as a suspect carcinogen by the National Institute of Occupational Safety and Health (NIOSH). It has been placed on the carcinogenic surveillance list of the American Conference of Governmental and Industrial Hygienists (ACGIH). The ACGIH TLV for dioxane is 50 ppm; the OSHA TWA is 100 ppm.

g/ Under Los Angeles County Rule 66, emissions of trichloroethylene were limited to 40 lb/day/piece of equipment. The EPA under the Clean Air Act of 1970 has recommended that Rule 66-type controls be implemented in those other geographic areas where trichloroethylene emissions are to be limited.

In a two-stage system, the part may be immersed in both the boiling liquid and the rinse liquid prior to rinsing in the vapor zone. In the event ultrasonic cleaning of the part is desirable, this modification may be made to the rinse chamber. Advantages of this system, in addition to the increased cleaning efficiency of multiple bath exposure, stem from increased efficiency in use of ultrasonics through solvent vapor loss control of the ultrasonically agitated liquid, once degassed.

The criteria for selecting candidates for vapor-degreasing systems are generally better defined than for cold-cleaning solvents and would include the following:[4-6]

- Nonflammable and nonexplosive.
- Low toxicity.
- Boiling point consistent with the temperature sensitivity of the material to be cleaned and the desired vapor zone cleanliness level.
- Low latent heat of vaporization.
- Low specific heat.
- High vapor density.
- Effective removal of ionic, nonionic, and particulate soils.
- Compatibility with materials to be cleaned.
- Stability of the system in the presence of water.

Some typical examples where chlorocarbons and chlorofluorocarbons are used in vapor-degreasing applications and the factors affecting the selection of the solvent are shown in Table VI-2.

2. Current use areas of F-113 and F-11: The very small current use of F-11 and F-112 is limited either to highly specialized, low volume applications or as a replacement for F-113 if it is unavailable to the user. Consequently, all discussions in this subsection will be directed towards F-113 with the understanding that, in certain isolated instances, F-11 or F-112 are used as a replacement. Azeotropes of F-113 and F-112 with other common solvents are also used; the specific azeotrope is dictated by the type of grease or other foreign material to be removed. Some of the common F-113 and F-112 azeotropes and blends, currently used for either vapor degreasing or cold-cleaning applications, are shown in the following list.

TABLE VI-2

TYPICAL APPLICATIONS FOR VAPOR-DEGREASING SOLVENTS[a]

Application	Solvent	Approximate Vapor Temp., °F	Factors Affecting Selection
Removal of oils, greases, and waxes from parts	Trichloroethylene	188	Most commonly used degreasing solvent.
Removal of high-melting oils, greases, and waxes	Perchloroethylene	250	Used where higher operating temperature is desirable.
Removal of water films from metals	Perchloroethylene	250	Rapid and complete drying in one operation.
	Freon TP 35	118	Used only at room temperature for drying and only when small quantities of water are to be removed.
	Freon T-DA 35/TF	NA	Used where large quantities of water are involved and spot-free drying is desired.
Cleaning coils and components for electric motors	Methyl chloroform[b]	165	Solvent must not damage wire coating or sealing agents. Selection should be based on preliminary trials.
	Trichlorotrifluoroethane	118	
	Perchloroethylene	250	
Cleaning temperature-sensitive materials	Trichlorotrifluoroethane	118	Used where parts must not be exposed to higher vapor temperature during cleaning.
	Methyl chloroform[b]	165	
Cleaning components for rockets or missiles	Trichloroethylene	188	Cleaned parts must be free of soils or residues that might react with oxidizers. White room cleaning.
	Perchloroethylene	250	
	Methyl chloroform[b]	165	
	Trichlorotrifluoroethane	118	
Cleaning with ultrasonics	Trichloroethylene	188	For cleaning efficiency beyond that obtained from standard vapor degreasing. Solvent must be kept clean by continuous distillation and filtration during use. Selection should be based on preliminary trials.
	Perchloroethylene	250	
	Methyl chloroform[b]	165	
	Trichlorotrifluoroethane	118	

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[a] Metal Progress, T. J. Kearney and C. E. Kircher, p. 93 (modified), May 1960.

[b] Use of methyl chloroform requires special equipment design and corrosion-resistant materials of construction.

Source: See Reference 4.

Vapor Degreasing Agents

Composition	Trade Name
32% F-112 + 68% isopropanol	Alpha 1001
85.5% F-112 + 14.5% *n*-propanol	Alpha 1003
F-113	Freon TF, Genesolv D
F-113 (elec. gr.)	Freon PCA, Genesolv D-elec. gr.
96% F-113 + 4% isopropanol	Genesolv DI
96.25% F-113 + 3.75% ethanol	Freon TE
95.5% F-113 + 4.5% ethanol	Genesolv DE
55% F-113 + 42% methylene chloride + 3% methanol	Genesolv DTA
50.5% F-113 + 49.5% methylene chloride	Freon TMC
89% F-113 + 11% acetone	Freon TA
94.05% F-113 + 5.7% methanol + 0.25% nitromethane	Freon TMS
40% F-113 + 51% methylene chloride + 9% cyclopentane	Genesolv DMC
95% F-113 + 5% acetonitrile	Genesolv DA
95.2% F-113 + 3.8% SDA-30 ethanol + 1.0% nitromethane	Freon TES

Cold-Cleaning Agents

Composition	Trade Name
90% F-113 + 10% isopropanol	Genesolv DS-10
65% F-113 + 35% isopropanol	Genesolv DI-35
64.7% F-113 + 35% isopropanol + 0.3% nitromethane	Freon T-P 35
90% F-113 + 10% SDA-30 ethanol	Freon T-E 10
85% F-113 + 15% SDA-30 ethanol	Genesolv DE-15
65% F-113 + 35% SDA-30 ethanol	Freon T-E 35
91.5% F-113 + 6% water + 2.5% surfactant	Freon T-WD602

The Alpha series are products of Alpha Metals, Inc.,[7] while the Freon series are produced by E. I. du Pont de Nemours and Company, Inc., and the Genesolv products are by Allied Chemical. The information shown above is for illustrative purposes only and is not intended to be a complete compilation. Its utility is to exemplify some of the numerous types of mixtures of F-112 and F-113 that are available commercially and the other components that are often added to the chlorofluorocarbons.

At the present time, the primary use of F-113 and its azeotropes is for the vapor degreasing and cleaning of components in the electrical and electronic industry. It is commonly used in systems where ultrasonics are employed in conjunction with the vapor degreasers or cleaners. Because it can be prepared with very high purity, has low toxicity, and possesses excellent material compatability, F-113 based materials are utilized in white-room metal cleaning applications. In addition, the low boiling point of F-113 (48°C) allows its usage with temperature-sensitive materials or component systems. A former major use of F-113 was in the aerospace industry but, since the termination of the Apollo program, limited quantities have been used in this application. However, spin-off industries generated during the space program, which depend on state-of-the-art technology, use F-113.

The major specific use area for F-113 is the flux removal and general cleaning of printed circuit boards (PCB) for the electronics industry. These solvents are well-suited for this application as they effectively remove the fluxes used in high volume production of machine soldered boards. These solvents are also well suited for flux removal following hand-soldering operations generally associated with PCB repair and rework. Other specific areas of application for F-113 and its azeotropes include:[8]

* Electronic relays
* Switches
* Potentiometers
* Electrical connectors
* Electrical motors
* Semiconductors
* Amplifiers
* Memory discs
* Integrated circuits
* Gyroscopes
* Accelerometers
* Precision valves
* Bearings
* Magnetic tape heads
* Vacuum tubes
* Nuclear power equipment
* Hydraulic systems
* Missile fuel systems

In addition to applications directed primarily at the manufacturing aspects, F-113 and its azeotropes are also used for in-place maintenance by spray cleaning while the equipment is completely assembled or in operation. Examples of such applications include:

* Electrical control panels
* Telephone switch gear
* Electrical motors
* Fork lift trucks
* Precision bearings

3. Alternative systems: The selection of substitute solvents or alternative cleaning procedures to replace the current chlorofluorocarbons (F-11 and F-113) is a difficult task due to the variety of unique cleaning and drying problems. Metal degreasing is an art that has achieved its present

state of development by trial and error methods of evaluation of the available solvents and aqueous surface active agents. In almost direct contrast to the other areas of application, the area of solvent cleaning and degreasing is much more of an art than a science.

The advantages and disadvantages, relative to F-11, F-112, and F-113, of some of the more common viable substitutes are discussed in Table VI-3.[6,8] Most of these solvent and degreasing systems are widely used at the present time and were the choice before being replaced in specific application by chlorofluorocarbons.

Formulations of alkaline cleaners and detergents for use in aqueous systems are complex mixtures of primarily inorganic compounds that are tailored to the specific application. Two typical formulations for unheated alkaline cleaning solutions are shown below:[9]

Component	% by Weight
Solution A	
Borax	28-30
Sodium tripolyphosphate	13-17
Sodium orthophosphate monohydrogen	8-12
Sodium carbonate, anhydrous	25-30
Sodium nitrite	6-12
Wetting agents	8-10
Solution B	
Sodium sesquicarbonate	27-33
Sodium pyrophosphate	27-33
Sodium tetraborate	18-22
Sodium nitrite	14-16
Polyoxyethylene glycol	2.9-3.1
Petroleum solvent	1.9-2.1

The variation in alkaline cleaner formulations for various metals with respect to the specific metal and the method of application is exemplified by the data shown in Table VI-4. From the data in this table and the above information, it is readily apparent that, while alkaline cleaners may be acceptable substitutes in certain applications, no single formulation will suffice and each application will require a specific formulation.

A review of the patent literature (via Chemical Abstracts) from 1967 to 1975 was conducted for new azeotropes and blends of chlorocarbons and/or chlorofluorocarbons with applications in the solvent degreasing field. The review revealed very few new systems and only one that did not incorporate either F-112 or F-113. A system of 35 to 58% perchloroethylene and the balance methylene chloride (CA, 79, 80658g, 1973) was patented for metal cleaning applications.

TABLE VI-3

COMMON SOLVENTS AND DEGREASING SYSTEMS AS POSSIBLE ALTERNATIVES

System	Application	Relative Advantages	Relative Disadvantages
F-113 CCl_2FCClF_2	a. Cleaning · Electronic parts · PCB · Relays and thermal switches · Computer discs · Electric motors · White room components · Optical lenses · Waveguides · Precision bearings · Hydraulic systems · Integrated circuits · Semiconductor devices · Business machines b. Drying · Coin blanks · Plated parts · Jewelery · Glass	· Nonflammability · Low toxicity · Chemically stable without inhibitors · Low surface tension · High liquid and vapor density · High purity · High dielectric strength · Recoverable by distillation and carbon absorption · Does not normally require venting	· High initial cost · Limited use as cold cleaning agent · Limited solvency · Low boiling point
Trichloroethylene $ClHC:CCl_2$	· Ultrasonic cleaning · Wool degreasing · Electronic parts cleaning · Solder flux removal · Electric motor cleaning and maintenance · Business machine cleaning · Flush solvent for liquid oxygen systems · Missile and rocket component cleaning (white room)	· Less expensive · Readily applicable to current equipment · High cleaning efficiency	· Photochemically reactive · Probable incompatibility with some plastics, elastomers, paints, etc. · High boiling point · TLV = 100 ppm · Reacts with sodium hydroxide to produce dichloroacetylene which is toxic and spontaneously combustible
Perchloroethylene $Cl_2C:CCl_2$	· Electronic parts cleaning · Solder flux removal (incomplete) · Optical lens cleaning · Wool scouring · Cleaning of electric motors and component parts · Ultrasonic cleaning · Missile and rocket (component cleaning (white room) · Component of proprietary solvents	· High boiling point permits metal drying, reduces staining, removes waxes, pitches and other gross high melting contamination · Stable to hydrolysis · Less expensive · Good solvent power (KB value of 90) · Best carbon adsorption recovery of chlorocarbons · May be operated in air-cooled equipment but not recommended	· Requires engineer to operate boilers for vapor degreasers (40-60 psig steam) · High heat input (steam) · High boiling point presents burn hazard, high solvent consumption, may warp or structurally change heat-sensitive parts · Requires special controls for aluminum alloys · Steam distillation causes water contamination · TLV = 100 ppm

TABLE VI-3 (Concluded)

System	Application	Relative Advantages	Relative Disadvantages
Methylene chloride CH_2Cl_2	· Thermal switches · Removal of photo-resistant ink (PCB) · Cleaning of temperature-sensitive equipment	· Highest solvent power for paint and varnish · Virtually unreactive under atmospheric conditions	· Incompatible with plastics, elastomers and paints · Low vapor density results in excessive solvent loss without a high freeboard · High evaporation rate · TLV = 100 ppm
Methyl chloroform CH_3CCl_3	· Removal of solder flux · Cleaning electrical coils and motors Cleaning office equipment · Cleaning temperature-sensitive equipment · Ultrasonic cleaning	· High solvent efficiency · Less expensive · Suitable for cold cleaning · May be used on PCB and hermetic stators, depending upon construction material	· Moderate boiling point · Requires good condensation system and temperature control · Carbon adsorption recovery system depletes stabilizers · Must be stabilized against hydrolysis · Cannot be used with gross water contamination · Photochemically reactive · Unstable in the presence of freshly machined aluminum
Aqueous systems Emulsion cleaners Alkaline cleaners Detergents Neutral synthetic cleaners	· Ultrasonic cleaning · PCB · Waveguides · Switch components · Instrument connector pins · Ring bearings · Vacuum tube cleaner · Coated and uncoated lenses	· Less expensive · Nontoxic · Removes both organic and inorganic contaminants · Almost complete material compatibility · Nonflammable	· Requires large operating areas · Requires multiple rinsing and dry oven · Increases process time · Presents potential for moisture and corrosion problems · Can present disposal problem; must be separated from water · Requires high energy input to heat or boil · Difficult to remove from blind holes, crevices, and densely packed printed circuits · Not applicable for military specification applications

TABLE VI-4

TYPICAL ALKALINE CLEANER FORMULATIONS FOR VARIOUS METALS[9]

	Aluminum		Copper			Cu Plate	Iron and Steel			Magnesium		Zinc		
	Soak	Spray	Soak	Spray	Electrolytic	Electrolytic	Soak	Spray	Electrolytic	Soak	Spray	Soak	Spray	Electrolytic
						Composition of Cleaner, % by Weight								
Builders														
Sodium hydroxide, ground	-	-	20	15	15	55	20	20	55	20	20	-	15	15
Sodium carbonate, dense	-	-	18	-	-	8	18	29	8.5	18	29	-	-	-
Sodium bicarbonate	21	24	-	34	34	-	-	-	-	-	-	-	35	34
Sodium tripolyphosphate	30	30	-	-	10	-	20	20	10	20	20	90	10	10
Tetrasodium pyrophosphate	-	-	20	10	-	10	-	-	-	-	-	-	-	-
Sodium metasilicate, anhydrous	45	45	30	40	40	25	30	30	25	30	30	-	40	40
Surface-Active (Wetting) Agents														
Sodium resinate	-	-	5	-	-	-	5	-	-	5	-	5	-	-
Alkyl aryl sodium sulfonate	3	-	5	-	-	-	5	-	1	5	-	5	-	-
Alkyl aryl polyether alcohol	-	-	2	-	-	1	2	-	-	2	-	-	-	-
Nonionics high in ethylene oxide	1	1	-	1	1	1	-	1	0.5	-	1	-	-	1
						Other Conditions								
Operating temperature of solution, °F	160	160	180	170	160	180	200	170	180	200	170	180	170	180
Concentration of cleaner, oz/gal H_2O	4	1	8	1	8	8	8	1	8	8	1	4	1	6

Additional chlorofluorocarbons and fluorocarbons are presently available in research quantities which may prove to be acceptable substitutes. It must be stressed that the suggested applicability of these materials is purely speculative and based on very limited available information. The materials discussed below are all products of E. I. du Pont de Nemours and Company but similar products may be available from other fluorocarbon manufacturers.

Perfluorodimethylcyclobutane (C51-12) has a boiling point of 113°F (45°C) and is a stable fluid for heat transfer. It is compatible with electrical insulation so that, if it has good solvency properties, it may be useful for electrical motor and components cleaning applications. Its use as a heat-transfer medium would indicate good thermal stability and compatibility with common metals.

Two other compounds, F-132a and Freon® E-1, may find application, based strictly on boiling points, as suitable solvents but no information is available with regard to their solvency powers or compatibilities with various materials. F-132a is 1,1-dichloro-2,2-difluoroethane and Freon® E-1 is the highly fluorinated ether, $CF_3CF_2CF_2OCHFCF_3$.

As stated earlier in this section, the identification of specific alternatives is very difficult because each cleaning or drying problem is unique. The chlorocarbons are still widely used in the degreasing and solvent field and may be acceptable substitutes in some applications presently employing the chlorofluorocarbons; however, there are cleaning problems where no acceptable substitutes for chlorofluorocarbons exist. Use of the chlorocarbons in defluxing and electronic cleaning, major industries, has been limited by solvent/electronic component compatibility problems arising from their higher boiling points and greater solvent power.

The initial conversion from chlorocarbons to chlorofluorocarbons was due to a combination of technical and aesthetic reasons. A major factor influencing the conversion of many systems from chlorocarbon to fluorocarbon was the concern for employee safety. Technical factors include situations where chlorocarbons resulted in residue contamination problems, compatibility problems, water spotting, and incomplete cleaning. Other factors included multistep cleaning procedures, cooling periods prior to handling of cleaned parts, higher rejection rates, and overall reduction in production volumes and increased labor costs. Increased emphasis on worker environment will necessitate the use of better vapor and liquid control measures should a return to the use of chlorocarbons occur. These increased control measures will result in additional capital outlay for new equipment. In addition to additional capital outlays, the increased control measures dictated by a conversion to chlorocarbon solvent systems will also result in increased solvent consumption and costs for chemical monitoring and control. Implementation of freeboard chilling systems or carbon adsorbers will deplete inhibiting systems commonly used in methyl chloroform and methylene chloride. Control of solvent vapors emitted from trichloroethylene and perchloroethylene degreasers will dictate the use of exhaust systems, with attendant loss and environmental problems. The lower cost of chlorocarbons as compared to chlorofluorocarbons should offset a portion of the monetary cost of control equipment. The amount of compensation will be determined by the adaptability of present equipment to the new solvent and the specific solvent application.

Other common solvents, such as ketones, alcohols, or hydrocarbons, are presently used in very small volume operations where a close control can be maintained on their utilization. Since essentially all of these solvents have low flash points and explosive limits, extreme caution would be necessary if their use were expanded or more generalized and would necessitate the use of very efficient vapor control and recovery equipment. Due to the inherent danger, flammable solvents are not considered to be acceptable alternatives. The observance of toxicity limitations would also be a factor in the utilization of these materials as in the case of the chlorocarbons. As with the chlorocarbons, no specific alternative can be suggested for widespread applicability since each degreasing operation presents its own set of circumstances.

The ultimate selection of an appropriate solvent obviously is not a well-defined situation. In some instances the widely used chlorocarbons may be acceptable alternatives, and in other cases the use of aqueous solutions of cleaners and detergents could be satisfactory. A major application of fluorocarbon solvents is the removal of rosin flux from printed circuits intended for military use. With the many different materials involved in the fabrication of printed circuits and the problem of qualifying a new solvent to meet military specifications, it is unlikely that a ready substitute is available. Our general assessment of this use category for chlorofluorocarbons is that substitute solvents and/or cleaning technology may be available for some applications presently employing chlorofluorocarbons, but due to the unique problems associated with each cleaning or drying problem, the considerations should be made on the basis of each individual use.

B. The Dry-Cleaning Industry

This area of application consumes very small quantities of chlorofluorocarbons in the United States. It was stated in the introdduction to this section that approximately 2 to 4 million pounds of F-113 were used in 1975 in the dry-cleaning industry, as compared to an estimated 400 million pounds of perchloroethylene. In Europe, F-11 is used as a dry-cleaning agent but not in the United States.

There are three basic types of dry-cleaning equipment systems: transfer type, dry-to-dry type, and coin-operated. A detailed discussion of dry-cleaning equipment and solvent mileage can be found in the Arthur D. Little Report.[1/]

Perchloroethylene can be used in all of the three equipment types. Fluorocarbon* 113 is used in dry-to-dry (often called "Valclene" machines) systems. Care is taken to minimize loss of F-113 because of its high cost. Petroleum distillates (Stoddard solvent and 140-F) are used in the transfer type (washer-extractor) systems. According to a recent survey of the International Fabricare Institute,[11/] the most commonly used systems are of the washer-extractor type.

1. General criteria required of a dry-cleaning solvent:[10,12/] To qualify as a dry-cleaning solvent, a candidate must possess certain physical and chemical characteristics. The National Institute of Dry-Cleaning has set seven general criteria for a dry-cleaning agent. These criteria are as follows:

a. The dry-cleaning agent must be safe to use on all common textile fabrics and dyes.

b. It must be a good solvent for fats and oils.

c. The candidate must be free of objectionable odors.

d. It must be chemically stable under all use conditions.

e. The dry-cleaning solvent should be noncorrosive towards ordinary metals used in machine, pipe and pump construction; it must also not swell or dissolve a wide range of plastics.

f. The candidate should be sufficiently volatile to permit economical reclamation by distillation and to permit rapid, economical, and safe drying conditions.

g. The solvent must also be compatable with a wide range of detergents so as to enhance its cleaning ability.

In conjunction with the above criteria, the solvent must be low in toxicity to minimize any hazard to the worker during processing and to the customer should residual solvent be left in the clothing. The solvent should have a flash point above 100°F (38°C) or should be nonflammable. The dry-cleaning agent should not bleed dyes or weaken, dissolve, or shrink textile fibers.[13/]

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* The term fluorocarbon designates both the fluorocarbons and the fluorochlorocarbons.

TABLE VI-5

COMMONLY USED DRY-CLEANING SOLVENTS[1,13-15]

Solvent	% Domestic Dry-Cleaning Market[a]	Flash Point (°C/°F)	Boiling Point (°C/°F)	Dry End Point (°C/°F)	Specific Gravity (°C/60°F)	Density lb/gal (25°C)	Aromatic Content Volume (%)	Corrosiveness	Heat of Vaporization (Btu/lb)	Toxicity TLV (ppm)	Odor	Color	Vapor Density (Air = 1.00)
Perchloroethylene	72	None	121/250	123/254	1.623	13.55	0	Slight on metal	90	100	Ether-like	Water white	5.5
Stoddard solvent	26	41/105	152/305	177/350	0.766	6.38	11.6	None	~ 500	200	Sweet	Water white	1.0
140-F		59/138	181/358	202/396	0.789	6.57	12.1	None	~ 500	200	Mild	Water white	1.0
Fluorochlorocarbons	2												
F-113[b]		None	48/118	NA[c]	1.576	13.16	0	None	63	1,000	Like CCl_4	Water white	6.3
F-11		None	24/75	NA	1.494	12.34	0	None	78.31	1,000	Slight ethereal	Water white	5.0
Trichloroethylene		32/90	87/189	NA	1.462	12.16 (20°/20°C)	0	None	NA	100	Chloroform-like	Water white	NA
Methylene chloride		None	40/104	NA	1.320		0	NA	142	250	Ether-like	Water white	NA
Methyl chloroform		None	75/165	NA	1.385	11.50	0	NA	NA	500	Chloroform-like	Water white	NA

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a/ MRI estimates based on data in References 2 and 3.
b/ Valclene® (E. I. du Pont de Nemours and Company trade name) = F-113 + 0.1% cationic detergent.
c/ NA = not available or not known.

2. Solvents currently used for dry-cleaning: Solvents commonly used in domestic dry-cleaning are within one of three chemical classes: petroleum distillates, chlorinated hydrocarbons, or chlorofluorocarbons.

a. Petroleum distillates: The two major petroleum distillates still used extensively in domestic dry-cleaning are Stoddard solvent and 140-F. Stoddard solvent is a water-white, basically odor free petroleum distillate with a flash point of 100°F while 140-F is a petroleum distillate solvent so named because its flash point is 140°F. In specialized equipment, 140-F can be used in locations where Stoddard solvent is not allowed. It is somewhat more expensive than Stoddard solvent and is slower drying. A summary of the physical properties of these petroleum distillates can be found in Table VI-5.[1,10/]

b. The chlorinated hydrocarbons: The major domestic dry-cleaning agent used is perchloroethylene. Perchloroethylene is nonflammable and safe for use with a wide range of textile fibers. However, many specialty items such as furs and leathers cannot be cleaned with perchloroethylene. In addition to perchloroethylene, there are three other chlorinated hydrocarbons used as dry-cleaning agents: trichloroethylene, methyl chloride, and methylene chloride. None of these are used in significant quantities in the United States, because of incompatability with many synthetic fibers (e.g., trichlorethylene tends to bleed dyes from acetate fabrics).[1/] Physical properties and additional information for the chlorinated hydrocarbon dry-cleaning solvents can be found in Table VI-5.

c. The chlorofluorocarbons: To date, only F-113 has been used domestically as a dry-cleaning solvent. F-11 is used only in Europe. E. I. du Pont de Nemours and Company offers a F-113/detergent combination, Valclene®. This compound is expensive in comparison to the petroleum distillage and chlorinated hydrocarbon solvent and is used primarily for specialty cleaning, i.e., furs and leather. The petroleum distillates can also be used as specialty cleaners but, unlike F-113, the petroleum solvents are flammable. Perchloroethylene is nonflammable but its solvent properties are too strong to function as a speciality cleaner.

3. Alternatives to the chlorofluorocarbon solvents: Only a very small segment of the dry-cleaning industry would be affected should further usage of F-113 not be allowed. Such discontinued use of F-113 would affect approximately 2% of the total market. In the event F-113 is regulated, other chlorofluorocarbons or the petroleum distillates could be used as specialty dry-cleaning agents. In the final processing of leather goods, it is possible to treat the leather finish in a manner that will allow the use of perchloroethylene as a cleaning agent.[16/] A solvent, having a Kauri-Butanol (KB) value in the range of 30 to 40 and satisfying the general criteria discussed previously in this chapter, would be suitable as a specialty item cleaner and function as an alternative for F-113.

As previously mentioned, many of the petroleum distillates can serve as dry-cleaning solvents for furs and leathers. The KB values of Stoddard solvent, 140-F, hexene, pentane, etc., vary between 27 and 45, thus making them possible alternatives to F-113 with respect to solvency power. The petroleum distillates are flammable and cannot be used in shopping center dry-cleaning establishments. This problem could be generally adverted by locating specialty cleaning operations in nonrestricted areas.

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VII. POTENTIAL RANKINE CYCLE USES

In June 1972, at the United Nations Conference on the Human Environment in Stockholm, Sweden, representatives of some 113 nations met to translate their environmental concerns into a plan for action to preserve and enhance the human environment. The Stockholm Conference set the stage for concerted world action to solve environmental problems of concern to both developed and developing nations. One of the results has been to establish a list of pollutants, in order of priority, that must be controlled. Table VII-1 shows that organochlorine compounds in the air ranks second in order of priority.[18]

One possible source of organochlorine compounds in the air is through losses from Rankine cycle turbines using chlorinated fluorocarbons as the working fluid. More specifically, F-11, F-12, F-13, F-112, F-113 and F-114 are potential causes for concern. These particular chlorofluorocarbons are sufficiently stable to pass through the lower atmosphere and interact with the ozone layer (under ultraviolet light).

A. End Uses

The use of vapor turbines operating on the Rankine cycle with fluorocarbons as the working fluid is somewhat limited at the present time but is anticipated to show future growth. An examination of the state of the art indicates that most of the fluorocarbon turbines are experimental models with a rating of a few hundred kilowatts. No large turbines are currently being marketed to handle fluorocarbons as the working fluid.

Attempts to use fluorocarbon turbines on a commerical basis began about 1955 in the United States and other developed countries like Japan and the Soviet Union. A list of some of the more important fluorocarbon turbines is presented in Table VII-2.

In addition to the end uses indicated in Table VII-2, several other uses may materialize in the near future. These end uses can be placed in the following categories:

1. Power Generation

a. Central station power plant

1. Use in conjunction with solar electric generating plant.
2. Use in conjunction with geothermal electric generating plant.
3. Use in conjunction with steam turbines in a dual cycle power plant.

TABLE VII-1

LIST OF PRIORITY POLLUTANTS DEVELOPED AT THE INTERGOVERNMENTAL MEETING ON MONITORING AT NAIROBI (1974)

Order of Priority	Pollutant	Medium
1	Sulfur dioxide plus suspended particulates	Air
	Radionuclides	Food
2	Ozone	Air
	DDT, Organochlorine Compounds	Biota, Man
3	Cadmium and compounds	Food, Man, Water
	Nitrates and nitrites	Drinking Water, Food
	NO and NO_2	Air
4	Mercury and compounds	Food, Water
	Lead	Air, Food
	Carbon dioxide	Air
5	Carbon monoxide	Air
	Petroleum Hydrocarbons	Sea
6	Fluorides	Fresh Water
7	Asbestos	Air
	Arsenic	Drinking Water
8	Mycotoxins	Food
	Microbial Contaminants	Food
	Reactive Hydrocarbons	Air

TABLE VII-2

RANKINE CYCLE TURBINES IN OPERATION USING WORKING FLUIDS OTHER THAN STEAM

Date of Completion	Country	Location	Purpose	Working Fluid	Scale of Turbine
1928-1950	U.S.	Various	Topping Cycle	Mercury	7.5-20 Mw
1961	U.S.	Trunkline Gas Company Houston, Texas	Pipeline Gas Compressor	R-11	472 KW
1966	Israel and Africa	Remote Locations	Water Pumping (solar collectors used for heat)	Monochlorobenzene	600 w
1966	Japan	IHI	200RT Turbo-Refrigerator Drive	R-11	190 KW
1967	USSR	Kamchatka	Geothermal Generating Unit	R-12	750 KW
1968	U.S.	-	Demonstration Purposes	Dowtherm A	6 KW
1968	Japan	Japan Gas Chemical Mizushima Plant	Refrigeration Power Generation for Chemical Plants	R-11	3,800 KW
1969	Japan	Iwataya Department Store (Kyushu)	800RT Turbo-Refrigerator Drive	R-11	475 KW
1971	France	-	Radar Relay Power (radioisotopic heat source)	Monochlorobenzene	4 KW

TABLE VII-2 (Concluded)

Date of Completion	Country	Location	Purpose	Working Fluid	Scale of Turbine
1975	U.S.	Currently Being Marketed Around the Country	Electricity Generation (fossil fired)	Toluene	100 KW
1975	U.S.	Sandia, Labs Albuquerque, New Mexico	Electricity-Generation	Toluene	40 KW

b. On-site power plant

   1. Use in conjunction with solar electric generating equipment.
   2. Use with fossil-fired boilers for apartments, motels, hospitals, and shopping centers.

2. Transportation

   a. Automobile power units
   b. Mobile home and recreational units
   c. Propulsion power for use with ships

3. Industry

   a. Pipeline gas compressor
   b. Use in a dual cycle unit for plant compressors
   c. Use with solar collectors for pumping applications

B. Criteria for Selection of Working Fluids

The choice of a working fluid depends on many factors, some of which have no thermodynamic significance. In order to make an intelligent decision as to the best working fluids for a specific end use, it is necessary to develop a set of selection criteria. The following criteria are applicable to all of the end uses previously discussed.

1. Stability: Thermal stability is the first criterion in choosing a working fluid. A practical working fluid must be stable against decomposition under prolonged heating in contact with conventional construction materials. Since thermal stability of a chemical substance diminishes with increasing temperature, this factor is usually the limiting parameter in the selection of a peak cycle temperature, and therefore limits the potential energy conversion efficiency of the Rankine cycle.

The products of thermal decomposition form noncondensible gases which accumulate in the condenser. This inhibits its performance and deteriorates the work output of the system. The acceptable rate of thermal decomposition will depend on whether the decomposition products are corrosive, and how easily they can be removed.

2. Flammability: The flammability of the working fluid is important because the turbine will operate near large boilers and high temperature steam pipes. However, as the fluorocarbon system will normally be

sealed, it is anticipated that this criterion can be relaxed slightly. Flammability need not necessarily be a prohibiting factor provided that adequate precautions are taken.

3. Corrosivity: Corrosion is one of the problems associated with the design and maintenance of any power plant. The corrosive properties of any new working fluid must be carefully evaluated before it is accepted for power plant application.

A particular problem of corrosion may result if the new working fluid should leak into the steam circuit where high purity is essential. Another problem is the possible contamination of the working fluid by steam, cooling water, or decomposition products. Because the turbine systems are hermetically sealed, it is expected that the corrosion criterion is somewhat eased in that all moisture and air can be eliminated initially from the system.

4. Freezing: For a system to operate satisfactorily over a wide range of ambient temperatures, it is essential that the working fluid freeze below the minimum ambient temperature encountered by a power system. In fact, it should have a freezing point well below the minimum ambient temperature in order to minimize the startup power requirement of a system containing a highly viscous fluid near its freezing point.

5. Critical temperature: It is essential to the operation of a Rankine cycle turbine that the working fluid not be heated above the critical temperature. This requirement may be the limiting parameter in the selection of a peak cycle temperature, and therefore limit the potential energy conversion efficiency of the cycle. A theoretical treatment by Horn and Norris[4/] indicates that the minimum acceptable critical temperature is approximately 340°F.

6. Toxicity: The chosen working fluid in the Rankine cycle turbine should, if possible, be nontoxic. However, mercury has successfully been used as a working fluid in a number of power stations since 1928. In a plant using a toxic working fluid, special precautions must be taken to avoid leakage. In order to decide on a toxicity limit it is necessary to compare the increase in the plant cost and difficulty of maintenance and operation against the advantages of using the toxic fluid.

7. Turbine size: A reduction in turbine size is desirable in order to reduce the cost and complexity of the turbine. This can be accomplished if the working fluid has a low specific volume and a high latent heat of vaporization. While there does not appear to be a specific size reduction that is considered to be "right," a reduction in the exhaust area of at least 4-5:1 is desirable.

An approximate idea of the relative machine size of different fluids can be obtained from basic fluid properties:4/

$$\text{Exhaust area ratio} = \frac{[M\ Pc\ Lc^{3/2}]_{\text{steam}}}{[M\ Pc\ Lc^{3/2}]_{\text{fluid}}}$$

where M = Molecular weight

Pc = Pressure of the vapor in the condenser

Lc = Latent heat of vaporization

8. Molecular weight: When a gas expands adiabatically, heat energy is convered into kinetic energy. This can be presented by $1/2\ V_2 = \Delta H$ (for a unit mass), where V_L is the velocity of the fluid leaving the turbine and ΔH is the heat drop. It can be shown thermodynamically that the ΔH obtainable from a fluid is inversely proportional to the molecular weight of the fluid. Thus, by choosing a working fluid of sufficiently high molecular weight, the exit velocity of the fluid can be reduced to the point where velocity or pressure compounding is unnecessary to reduce the turbine blade speed to practical limits. It is best if the molecular weight of the fluid exceeds 100.

9. Boiling point: The boiling point of the working fluid has a considerable influence on its performance in a turbine. The most important influence is the disc and blade function. It can be shown that the friction of the turbine is proportional to the vapor pressure in the condenser. Therefore, the friction can be reduced by having a fluid with a low vapor pressure, i.e., a high boiling point vapor. A cautionary note should be added: the fluid should not have too low a vapor pressure to avoid high vacuums in the condenser. A vapor pressure range of 1 to 15 psi is desirable.

10. Temperature - entropy diagram: The T-S diagram for water shows that the slope of the vapor-liquid line is negative. This means that when saturated steam expands isentropically, the steam becomes wet. If this wetness exceeds a certain amount, it can cause erosion of the turbine blades.

Wetness loss is a purely practical issue not predicted by theory and only discoverable in its amount by careful testing. It is not known whether fluids other than steam exhibit wetness loss, but there is no reason to suppose that they would not. The wetness loss in steam is about 1% loss of stage efficiency for each 1% of water present. For a steam turbine this loss amounts to approximately 6%.

It is desirable to select a working fluid which has a slightly positive vapor-liquid line on the T-S diagram. This assures that the fluid expands into a dry region as it passes through the turbine. Both erosion of the turbine blades and wetness loss will be decreased.

11. Number of atoms/molecule: The cycle efficiency of the Rankine cycle can be improved if, by a judicious selection of working fluid and cycle conditions, the turbine exhaust lies on the saturation curve (vapor-liquid line). This offers the joint advantages of requiring very little superheat to avoid wetness losses, and very little regenerative heating is necessary. Consequently, fluids are desired which have a nearly vertical vapor-liquid saturation line.

Theoretical studies have shown that the slope of the vapor-liquid boundary is a function of the number of atoms in the molecule. Molecules with a small number of atoms would have T-S diagrams similar to water, while molecules with a large number of atoms would have a strongly positive slope. A vertical T-S diagram calls for a rather small number of atoms, 5 to 10. Combining a small number of atoms with a high molecular weight requires heavy atoms such as chlorine or bromine.

C. Identification of Possible Alternate Working Fluids for Rankine Cycle Engines

Having identified the possible end uses of Rankine cycle turbines using working fluids other than steam, and the criteria for selection of acceptable fluids, candidates for use in these engines were identified. A large number of possible fluids were considered. However, where the published literature indicated that a fluid was undesirable because of instability, corrosiveness, etc., it was rejected from further consideration.

Table VII-3 presents a partial list of viable candidates for use in a Rankine cycle turbine. All of these fluids have been evaluated by other researchers during various studies.[1-17]

The first group of six fluids represents the chlorinated fluorocarbons which are to be considered banned. These fluids were included to serve as a basis against which to measure the properties of the alternate fluids (second group). The third grouping consists of alternate halogenated compounds. It is not entirely certain that these alternate halogenated compounds offer any advantage over the first group. Careful testing of the stability of each compound will be required to determine the danger to the ozone layer.

The properties of each alternate fluid were obtained from various sources and may not reflect the latest available data. However, the numerical values are sufficiently accurate to permit use of the selection criteria.

TABLE VII-1

ALTERNATIVE WORKING FLUIDS FOR RANKINE CYCLE ENGINES

Fluid	Formula	Molecular Weight	Boiling Point (°F) (1 atm.)	Freezing Point (°F)	Critical Temperature (°F)	Liquid Density (lb/ft^3)	Vapor Density (lb/ft^3)	Latent Heat of Vaporization (Btu/lb)	Slope of Vapor Pressure Curve	Toxicity	Flammability
F11	CCl_3F	137.4	74.9	-168.0	388.4	92.1	0.367	78	+	5a	A
F12	CCl_2F_2	120.9	-21.6	-252.0	233.6	81.8	0.395	71	+	6	A
F13	$CClF_3$	104.5	-114.6	-294.0	83.9	81.1	0.438	64	+	6	A
F112	CCl_2F-CCl_2F	203.8	199.0	79.0	532.0	102.1	0.438	67	+	4-5	A
F113	$CCl_2F-CClF_2$	187.4	117.6	-31.0	417.4	97.7	0.461	63	+	4-5	A
F114	$CClF_2-CClF_2$	170.9	38.8	-137.0	294.3	90.9	0.489	57	+	6	A
Water	H_2O	18.0	212.0	32.0	705.0	62.4	0.037	1,050	-	6	A
Ammonia	NH_3	17.0	-28.0	-107.9	271.4	42.6	0.056	589	=	2	B
Ethane	C_2H_6	30.0	-127.5	-297.0	90.0	7.6	0.129	212	=	5b	D
Propylene	C_3H_6	42.1	-53.7	-301.0	197.2	2.2	0.147	191	+	4-5	D
Propane	C_3H_8	44.0	-44.2	-305.8	206.3	6.8	0.145	182	+	5b	D
Butane	C_4H_{10}	58.1	31.3	-211.0	306.0	5.8	0.167	166	+	5b	D
Isobutane	$(CH_3)_3CH$	58.1	10.0	-229.0	273.0	37.6	0.175	158	+	5b	D
Benzene	C_6H_6	78.0	176.0	41.0	552.0	54.8		175	+	4-5	D
Biphenyl	$(C_6H_5)_2$	154.2	492.6	159.8	961.0	56.1			-	1	B
Toluene	$C_6H_5CH_3$	92.0	230.0	-139.0	605.4	49.9		153	+	4-5	D
Ethyl Ether	$C(C_2H_5)_2$	74.1	94.3	-177.2	381.0	44.5		153		4-5	D
Trimethylisobutene	$(CH_3)_2CHCH:CH_2$	70.0	172.2	-165.7	341.0	44.0		150			C
MIPB	$C_{15}H_{16}$	196.0	560.0	-68.0					+		
Orthoxylene	$C_6H_4(CH_3)_2$	106.0	291.2	-16.6	675.0	54.9		151	-		
Ethylene Oxide	C_2H_4O	44.0	51.3	-169.1	381.0	56.0		240		4	B
Methyl Formate	$HCOOCH_3$	60.0	89.2	-146.2	418.0	61.2	0.145	200		3	B-C
Acetaldehyde	CH_3CHO	44.0	68.4	-190.3	370.0	48.9		245		1	B-C
Methyl Mercaptan	CH_3SH	48.0	42.7	-189.4	361.0	53.7		230		4-5	D
Ethylamine	C_2H_5NH	45.0	61.9	-217.7	369.0	57.6		159		1	C
Dowtherm A	$26.5\%(C_6H_5)_2/$- $73.5\%\ (C_6H_5)_2O$		495.8	53.6	930.0	66.0			-	5b	B
Carbon Dioxide	CO_2	44.0	-109.0 (76.4 psi)	-69.6	87.8	97.6	0.176	256.3	=	5a	A
Sulfur Dioxide	SO_2	64.0	14.0	-104.0	315.0	91.2	0.192	172.3	=	1	A
Mercury	Hg	200.6	672.0	-38.0	2,800.0	845.2	0.048	125	-	1	A
Potassium	K	39.1	1,400.0	147.0	3,951.0	44.6	0.031	892		1	D

TABLE VII-1 (Concluded)

Fluid	Formula	Molecular Weight	Boiling Point (°F) (1 atm.)	Freezing Point (°F)	Critical Temperature (°F)	Liquid Density (lb/ft^3)	Vapor Density (lb/ft^3)	Latent Heat of Vaporization (Btu/lb)	Slope of Vapor Pressure Curve	Toxicity	Flammability
F14	CF_4	88.0	-198.0	-299.0	-50.2	82.2	0.476	58	=	6	A
F21	$CHCl_2F$	102.9	48.1	-211.0	353.3	85.3	0.285	104	+	4-5	A
F22	$CHClF_2$	86.5	-41.4	-256.0	204.8	74.5	0.295	100	+	5a	A
F23	CHF_3	70.0	-115.0	-247.0	78.0	42.0	0.291	103		6	
F115	$CClF_2$-CF_3	154.5	-38.4	-159.0	175.9	80.6	0.322	54		6	A
F116	CF_3-CF_3	138.0	-108.0	-149.0	67.0	99.0	0.362	50		6	
F114B$_2$	$CBrF_2$-$CBrF_2$	259.8	117.1	-166.8	418.1	135.0		45		5a	
F-C318	C_4F_8	200.0	21.0	-42.0	239.0	94.0	0.601	50	◆	5a	
FC-75	$C_8F_{16}O$	416.0	212.0	-76.0	460.0	110.5		35	◆		A
Dibromodifluoromethane	CBr_2F_2	210	76.1					32			A
Ethyl Chloride	C_2H_5Cl	64.5	54.0	-217.7	369.0	57.6		139		4-5	C
Methylene Chloride	CH_2Cl_2	84.9	105.2	-142.0	421.0	82.8	0.209	142	-	4-5	A
Methyl Chloride	CH_3Cl	50.5	-10.8	-144.0	289.6	62.6	0.162	180	o	4	C
Methyl Bromide	CH_3Br	95.0	38.2	-136.6	376.0	108.1		110		2	B
Boron Trichloride	BCl_3	117.2	54.5	-160.6	356.0	89.5		67		4-5	
Hexafluorobenzene	C_6F_6	186.0	196.0	-67.0	471.2	100.3			=		A
Monochlorobenzene	C_6H_5Cl	112.5	269.6	-49	678.2			160	=	4-5	D
Tribromofluorosilane	Br_3FSi	289.0	185.0	-112.0					=	6	
RC-1	C_6F_6, C_6HF_5	175.3	172	-44	480.0	96.7	0.376	79	+	4-5	A
RC-2	$H_2O_1HC_5H_5CH_3$	44.3	200	-40	675.0	61.5	0.904	378	-	5b	B

Both the toxicity and flammability of each alternate working fluid are presented in somewhat qualitative terms in Table VII-3. Table VII-4 is a semiquantification of the toxicity of each fluid based on the classification used by Underwriters Laboratory. Table VII-5 is a definition of the classification of the comparative flammability of various vapors.

D. Advantages and Disadvantages of Selected Working Fluids for Rankine Cycle Turbines by End Use

The following discussion presents the relative advantages and disadvantages of selected working fluids for Rankine cycle turbines by specific end use. It is extremely unlikely that one particular fluid will be found which will satisfy all of the requirements for each application. Tables VII-3 through VII-5 illustrate this point by showing that, although some fluids may be ideally suited for a compact turbine or for heat exchanger design, they are completely unsuitable on chemical grounds. This situation suggests that the final selection of one particular fluid for each application will be difficult. The decisions may well rest on features such as toxicity, flammability, or stability.

The conclusion reached as a result of this analysis is that the "best" working fluid will be chosen based on the specific purpose of the turbine, and on the turbine design. Therefore, it is not a useful exercise to attempt to indicate the reasons for the rejection of all other working fluids. Rather, the following analyses are generic in nature, and present only the advantages and disadvantages of the most promising candidates for selection within each end use category.

1. Power generation

a. Benzene: The advantages of benzene as a working fluid in a Rankine cycle turbine are:

* Excellent stability.

* Low to moderate toxicity.

* Noncorrosive.

* Satisfactory low temperature startup capability.

* T-S diagram has a positive slope to the vapor-liquid line (expands into dry region).

* Reduction in turbine exhaust area compared to steam turbine is approximately 15.

TABLE VII-4

UNDERWRITERS' LABORATORIES CLASSIFICATION OF COMPARATIVE HAZARD TO LIFE OF GASES AND VAPORS

Group	Definition
1	Gases or vapors which in concentrations of about 1/2 to 1% for duration of exposure of about 5 min are lethal or produce serious injury.
2	Gases or vapors which in concentrations of about 1/2 to 1% for durations of exposure of about 1/2 hr are lethal or produce serious injury.
3	Gases or vapors which in concentrations of about 2 to 2-1/2% for durations of exposure of about 1 hr are lethal or produce serious injury.
4	Gases or vapors which in concentrations of about 2 to 2-1/2% for durations of exposure of about 2 hr are lethal or produce serious injury.
Between 4 and 5	Appear to classify as somewhat less toxic than Group 4.
	Much less toxic than Group 4 but somewhat more toxic than Group 5.
5a	Gases or vapors much less toxic than Group 4 but more toxic than Group 6.
5b	Gases or vapors which available data indicate would classify as either Group 5a or Group 6.
6	Gases or vapors which in concentrations up to at least about 20% by volume for durations of exposure of about 2 hr do not appear to produce injury.

TABLE VII-5

CLASSIFICATION OF COMPARATIVE FLAMMABILITIES OF VARIOUS GASES AND VAPORS

Group	Definition
A	Nonflammable
B	Small Flammability Range
C	Large Flammability Range
D	Dangerous

- Molecular weight is < 100, but greater than water.

- Satisfactory condensor pressure.

The disadvantages of benzene as a working fluid in a Rankine cycle turbine are:

- Dangerously flammable - must use an inert gas system for sealing turbine shaft, etc.

- High freezing point - this can be overcome if the turbine is located inside a heated structure.

- Moderate value of critical temperature may limit use in some design applications.

- Heat transfer properties are not as good as water - this means that boiler and heat exchanger sizes are large.

- Maintenance on turbines, pumps, condensor, valves, etc., will have to be handled carefully due to the flammability factor.

b. Toluene: The advantages and disadvantages of toluene as a working fluid in a Rankine cycle turbine are similar to those of benzene with the following changes:

- The freezing point of toluene is such that system freezing is not a problem.

- The molecular weight of toluene is higher than that for benzene.

- A slightly higher critical temperature permits higher temperatures in the operating cycle.

c. Monochlorobenzene: The advantages and disadvantages of monochlorobenzene as a working fluid in a Rankine cycle turbine are similar to those of benzene with the following changes:

- Stability is not quite as good as benzene.

- The freezing point of monochlorobenzene is such that system freezing is not a problem except in extreme environments.

- The molecular weight of monochlorobenzene is satisfactory.

- A higher critical temperature permits higher temperatures in the operating cycle.

- T-S diagram has a vertical slope to the vapor-liquid line (expands along saturation line).

- Unacceptable costs at the present time.

d. FC-75: The advantages of FC-75 as a working fluid in a Rankine cycle turbine are:

- Chemically inert.

- Excellent stability.

- Noncorrosive.

- Nonflammable.

- Very high molecular weight.

- Satisfactory low temperature startup capability.

- T-S diagram has a positive slope to the vapor-liquid line (expands into dry region).

- Satisfactory condensor pressure.

- Satisfactory boiling and freezing temperatures.

The disadvantages of FC-75 as a working fluid in a Rankine cycle turbine are:

- Low critical temperature may severely limit use in power plant applications.

- Poor heat transfer characteristics may result in large heat exchangers.

- Low heat of vaporization.

- Unacceptable costs at the present time.

e. Ammonia: The primary advantages of ammonia as a working fluid in a Rankine cycle turbine is:

- Acceptable for use with low temperature cycles such as are encountered in solar electric power plants.

The disadvantages of ammonia as a working fluid in a Rankine cycle turbine are:

- High toxicity.
- Low molecular weight.
- Reacts with moisture.
- Flammability.

f. Mercury: The advantages of mercury as a working fluid in a Rankine cycle turbine are:

- Excellent stability.
- Nonflammable.
- Extremely high critical temperature puts no limit on the cycle operating temperatures.
- High molecular weight.
- Boiling point and freezing point are acceptable.
- Extremely high cycle efficiency because of the high temperature applications (topping cycles).
- Extensive operating experience with mercury as the working fluid.

The disadvantages of mercury as a working fluid in a Rankine cycle turbine are:

- Highly toxic - must prevent leakage from turbine shaft, etc.
- Maintenance on turbines, pumps, condensers, valves, etc., will have to be handled carefully due to the toxicity factor.
- Requires that austenitic steel be used to avoid corrosion problems.
- Condensing temperature cannot be below about 400°F due to vapor pressure considerations - this limits the use in some power plant applications.

* T-S diagram has a negative slope to the vapor-liquid line (expands into a wet region). The terminal wetness at the turbine exhaust is approximately 20%, thus causing significant erosion of the turbine blades.

2. Transportation

a. Monochlorobenzene: The advantages and disadvantages of monochlorobenzene as a working fluid in a Rankine cycle engine for use in transportation are the same as in the discussion on power generation, with the following exceptions:

* Monochlorobenzene is mildly toxic such that containment following an accident must be considered during design.

* The extreme flammability of monochlorobenzene makes it similar to gasoline, with the result that this factor must be considered a potential problem.

* Mild steel is attached by monochlorobenzene at elevated temperatures > 600°F.

b. Toluene: The advantages and disadvantages of toluene as a working fluid in a Rankine cycle engine for use in transportation are the same as in the discussion on power generation, with the following exceptions:

* Toluene is mildly toxic such that containment following an accident must be considered during design.

* The extreme flammability of toluene makes it similar to gasoline, with the result that this factor must be considered a potential problem area.

c. RC-1 (60 mole % pentafluorobenzene - 40 mole % hexafluorobenzene): The advantages of RC-1 as a working fluid in a Rankine cycle engine are:

* Excellent stability.

* Low to moderate toxicity (uncertain).

* Noncorrosive.

* Satisfactory condenser pressure.

* Nonflammable.

- * High molecular weight.
- * The freezing point of RC-1 is such that system freezing is not a problem except in extreme environments.
- * T-S diagram has a positive slope to the vapor-liquid line (expands into dry region).

The disadvantages of RC-1 as a working fluid in a Rankine cycle engine are:

- * Low heat of vaporization leads to high flow rates.
- * Low cycle efficiency leads to low miles per gallon.
- * Unacceptable costs at the present time.

d. RC-2 (65 mole % water - 35 mole % 2-methylpyridine):

The advantages of RC-2 as a working fluid in a Rankine cycle engine are:

- * Low to moderate toxicity.
- * Satisfactory condensor pressure.
- * High latent heat of vaporization.
- * Only slightly toxic (similar to LP gas).
- * The freezing point of RC-2 is such that system freezing is not a problem except in extreme environments.
- * T-S diagram has a positive slope to the vapor-liquid line (expands into dry region).
- * Higher cycle efficiency than RC-1 (higher miles per gallon).
- * Lower cost than RC-1.

The disadvantages of RC-2 as aa working fluid in a Rankine cycle engine are:

- * Moderate flammability (less than conventional fuels).
- * Low molecular weight.
- * Corrosive to mild steel.

3. Industry

a. Monochlorobenzene: The advantages and disadvantages of monochlorobenzene as a working fluid in a Rankine cycle turbine for use in pumping are the same as in the discussion on power generation.

b. Methylene chloride: The advantages of methylene chloride as a working fluid in a Rankine cycle turbine for use in operating a compressor are:

- Excellent stability at temperatures below 550°F.
- Low to moderate toxicity.
- Noncorrosive (particularly to aluminum).
- Satisfactory condenser pressure.
- Nonflammable.
- Molecular weight moderatley high.
- The freezing point of methylene chloride is such that system freezing is not a problem.

The disadvantages of methylene chloride as a working fluid in a Rankine cycle turbine are:

- T-S diagram has a negative slope to the vapor-liquid line (expands into wet region).
- Moderate value of critical temperature may limit use in some applications.

c. Toluene: The advantages and disadvantages of toluene as a working fluid in a Rankine cycle turbine for either pumping or operating a compressor are the same as in the discussion on power generation.

d. Benzene: The advantages and disadvantages of benzene as a working fluid in a Rankine cycle turbine for either pumping or operating a compressor are the same as in the discussion on power generation.

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VIII. DIRECT ECONOMIC CONSEQUENCES OF LIMITATIONS ON CHLOROFLUOROCARBONS

This chapter focuses on the primary economic effects that would occur if limitations on the use of selected chlorofluorocarbons necessitated the adoption of alternative chemicals or devices. These consequences include the direct costs to industries that currently use, or make products that use, these chlorofluorocarbons, and the costs to the consumer that purchase products or services that are currently based on chlorofluorocarbon technologies. Economic impacts will be analyzed for refrigeration, aerosol, foam blowing and solvent cleaning applications of the selected chlorofluorocarbons.

A. Refrigeration

Costs associated with the use of substitute chemicals and alternative refrigeration systems are considered in the following sections.

1. Substitute refrigerants: Few plausible chemical substitutes for R-11 and R-12 have been identified for use in mechanical vapor compression (MVC) refrigeration and air conditioning systems. Ammonia, sulfur dioxide, hydrocarbons and chlorinated hydrocarbons are technically feasible substitutes for the above chlorofluorocarbons; toxicity, flammability, materials compatibility problems, and the necessity for systems redesign are likely to preclude any substantial conversion to the use of such materials as refrigerants.

The most plausible substitutes for R-11 and R-12 as refrigerants appear to be R-22 and R-502, even though designs and hardware for using these refrigerants in home appliances and automotive refrigeration units are not available at present. Redesign and retooling costs of converting to R-22 for these end uses can be only crudely estimated.

A few major manufacturers of home appliances have given estimates for the costs of redesigning and retooling their own production lines varying from $10 to $50 million. When the number of production lines operated by each of the manufacturers is taken into consideration, this equates to about $10 million per production line. These numbers are admittedly crude because of a lack of available design data, and because of the reluctance of manufacturers to develop such data (they fear a possible future banning of the use of R-22 or R-502 in MVC refrigeration systems). While the costs of redesign and retooling appear to be quite high, they would ultimately be passed on to consumers in the form of higher unit prices. Such costs might have an adverse short-term economic impact, but little long-term economic impact on the refrigeration industry. Some of the smaller appliance manufacturers might be placed in serious economic jeopardy by the need for redesign and retooling capital. The appliance industry is very competitive, and operates on a relatively small margin, a fact which would be to the further disadvantage of the smaller manufacturers.

The conversion of existing R-12 appliances to R-22 would be prohibitively expensive if not technically unfeasible. No estimates are available for the cost of retrofitting existing units, but they could be more per unit than its current value. If further changeover were made through attrition, manufacturers would have to develop and maintain a parts inventory for both types of units, over an estimated 20-year period from the time R-12 was banned. Again, no estimates of the cost of maintaining such an inventory are available.

The average refrigerator requires 0.65 lb of refrigerant, while a freezer requires about 1.25 lb. Assuming that the average unit charge of refrigerant would be the same as for R-12 and R-22, the added cost of refrigerant per unit would be about \$0.50 for a freezer and \$0.25 for a refrigerator. However, since R-22 has a somewhat greater cooling capacity than R-12, less refrigerant may be required--thus reducing this cost differential. Such costs are nearly insignificant, assuming an average retail price of \$300 to \$400 for an appliance unit. It is apparent, therefore, that a suitable substitute refrigerant costing 10 or 20 times as much as R-12 would have only a small relative impact on the price of appliances. The cost of recharging a defective unit in place with a higher priced substitute would be proportionately, somewhat higher to the consumer, but the substantial cost of the service call greatly reduces the direct impact.

To convert future units from R-12 to R-22, one major home appliance manufacturer, who supplies over 20% of the appliance market, estimated that the redesign and retooling cost of \$50 million for retooling their plants would translate into an added cost of \$5/unit to the consumer.

Obviously, costs to some of the larger manufacturers would be less than those to smaller manufacturers. Taking all factors into consideration, we believe that an average appliance will increase in consumer cost by \$2 to \$10--depending on the make and model. This range translates to a 1 to 3% increase in price.

Comparative energy efficiencies have been estimated for various end-use products. Such efficiencies vary, however, with the intended use, size, and other design parameters. For example, comparative refrigerant performance per ton based on 5°F (-15°C) evaporation and 86°F (30°C) condensation indicates that R-22 requires a compressor horsepower of 1.011 as compared to 1.002 for R-12. Such a small change in energy efficiency would have a far greater economic impact when accumulated over the lifetime of the product than would the initial unit cost. Higher operating pressures and temperatures of R-22 units would also significantly reduce reliability, and result in higher maintenance and repair costs.

Substitution of R-22 or R-502 for R-12 in mobile air conditioners would also require design and retooling of production lines. One industry source estimated that an add-on auto air conditioner using R-22 would cost about 7% more than the current R-12 unit. It has been suggested that low-horsepower automobiles may not have sufficient power to handle R-22 refrigerant systems--indicating that energy requirements for R-22 systems are greater than for R-12 systems, and again posing the possibility that long-term operating costs would be significantly greater with the substitute.

Percentage increases in the manufacturing and consumer costs for dehumidifiers, water coolers, beverage refrigeration, and similar type units are estimated to be lower than those of the major home appliances, because existing applicable R-22 technology and hardware are available. The costs for ice-makers, however, would be comparable to those for refrigerators and freezers.

R-22 is currently used in some large cooling units. Consequently, design and retooling costs should not be as great as for the home appliances and other systems in which R-12 is used almost exclusively. However, operating efficiency and unit reliability would be of even greater importance. No information was developed on relative operating efficiency of such units. The higher operating pressures and temperatures would probably again result in reduced reliability and higher repair costs.

2. Alternative refrigeration systems: Absorption refrigeration systems could replace MVC units for many home appliance uses and in many industrial applications, i.e., ammonia-water systems for low-temperature operations and the lithium bromide-water system for higher-temperature applications.

Absorption refrigeration units currently account for only a small fraction of these markets (3.3% of the appliance market--mostly mobile home and recreation vehicles--and 1.25% of the air conditioning and chiller market). While the initial investment in such units is 50% higher than for a comparable MVC unit, operating costs have been lower primarily because of prices for natural gas (the energy source most commonly used for such units) have been unrealistically low. Recent rises in natural-gas prices have reduced the operating cost differential between the two types of units and further rises are possible. Absorption units deliver approximately 1.5 Btu of cooling per watt hour of energy input compared to approximately 3.0 Btu of cooling per watt hour of energy input for MVC units. Thus, absorption refrigeration is only half as energy-efficient as MVC refrigeration; however, under specific circumstances, the use of "waste" heat may provide an opportunity to reduce the energy input.

The poor energy efficiency alone will be a strong deterrent to substitution of absorption for MVC refrigeration, particularly when we consider that consumers typically pay $20 to $80/year for electricity to operate a vapor-compresson refrigerator-freezer.

Absorption units have little or no anticipated utility for automotive usage because of their size, unit weight, and higher energy requirements. They might have utility for large mobile units, but again energy costs would be a strong deterrent.

Absorption units currently account for about 2% of sales of chillers, based on tonnage (100 to 1,200 ton units), and cost about twice as much as MVC units. Rising energy costs and the lower energy efficiency of absorption units will be an even greater deterrent to their substitution for MVC systems in these larger units than in home-appliance applications.

Steam-jet refrigeration is used primarily where waste steam is available. The unit is less expensive and more maintenance-free than MVC systems. It is most useful for higher-temperature applications such as chillers or air conditioning. This system is probably competitive with MVC only in industrial applications.

Thermoelectric refrigeration, because of its high initial and operating costs and its need for direct current, offers little prospects for replacing MVC refrigeration systems in the foreseeable future.

The conventional air-cycle refrigeration systems used for aircraft and remote military operations likewise offer little or no prospect for replacing MVC refrigeration systems because of their inherent low efficiency.

A relatively new refrigeration system (the Rovac system), described by its developer as a "multifluid mixed phase cycle which is a hybrid of the reverse Brayton cycle and the reverse Rankine cycle," is currently in the prototype stage. The system is claimed to be technically feasible for a wide range of applications, including automobile air conditioners, transport refrigeration, home appliances, residential air conditioners and possibly commerical chillers.

Data on a prototype automobile air conditioner is said to show that the unit compares favorably to the conventional automobile air conditioner; it is only 32% as heavy, is 1.7 times as efficient, and will cost only two-thirds as much according to the manufacturers. Although these claims are impressive, additional development and testing is needed to demonstrate reliability and end-use applicability of this system.

B. Aerosols

Typical chlorofluorocarbon propelled aerosols use 0.3 to 0.4 lb of propellant per unit. Of the many types of products dispensed as aerosols, a few hair sprays, antiperspirants and deodorants, medicinals and pharmaceutical, colognes and perfumes, pan sprays, and a few other specialty items rely almost exclusively or chlorofluorocarbons as propellants.[1/] In all but a few cases alternative methods of delivering these products are available and on the market. These include the use of carbon dioxide and hydrocarbons as the propellant and mechanical applicators.

While mechanical delivery systems do not produce identical results to the chlorofluorocarbon-propelled aerosol products, they are generally less expensive and have obtained a degree of consumer acceptability. Table VIII-1 shows the types of products predominantly propelled with chlorofluorocarbons, the number of units sold annually, the costs of the delivery systems (excludes cost of active ingredient concentrate and solvents), the costs of using F-22 or FC-318 as propellants and estimated costs of viable alternative delivery systems. Candidate substitutes F-22 and F-C318 currently cost about 1.5-times and 10-times as much, respectively, as F-11 or F-12.

The number of applications of the product per unit package provided by the various delivery systems are uncertain. Therefore, the cost data presented in the table assumes equal numbers of applications for the aerosol and mecnanical applicators, although it appears that most mechanical delivery systems would provide a substantially larger number of applications per unit, thus making them even more economically favorable per unit application.

TABLE VIII-1

COMPARATIVE COST OF ALTERNATIVE DELIVERY SYSTEMS[1,3-5]

(Excludes Cost of Active Ingredient Concentrate)

Product Types	Millions of Units Filled (1974)	Percent Propelled by Fluorochlorocarbons	Average Weight Propellant/Unit (lb)	Estimated Cost of F-11 or F-12 Delivery System	Average Cost of Carbon Dioxide Delivery System	Estimated Cost of F-22 Delivery System	Estimated Cost of FC-318 Delivery System	Cost of Mechanical Delivery System[a]
Personal Products								
Hair Care	460	95	0.40	39¢	28¢	41¢	173¢	(1) 26¢ (4) 35¢
Antiperspirants and Deodorants	595	95	0.40	39¢	28¢[b]	43¢	192¢	(1) 27¢ (2) 11-12¢ (4) 35¢
Medicinal and Pharmaceutical	70	90	0.32	36¢	26¢	46¢	140¢	(1) 26¢ (3) 8¢ (4) 35¢
Colognes and Perfumes	145	95	0.05	15¢	14¢[c]	15¢	36¢	(1) 27¢ (4) 35¢
Pan Sprays	30[d]	95-98	0.52	49¢[e]	Applicability Unknown	48¢	278¢	(1) 26¢ (4) 35¢

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[a] The specific mechanical system(s) viable as alternatives are coded as follows:
(1) Mechanical spray pumps;
(2) Sticks, creams, and roll-ons;
(3) Collapsible tubes; and
(4) Bladder system, high pressure inner liner. Cost includes container system, valve, and cap where applicable.

[b] CO_2 is a viable propellant only for deodorants.

[c] Feasibility unknown with glass containers; price estimate assumes use of present containers.

[d] MRI estimate based on data from Reference 1 and communication with an industry source (2/76).

[e] F-114 serves as the propellant in pan sprays.

Chlorofluorocarbons may afford distinct advantages over other delivery systems for a few products, primarily medicinals and pharmaceuticals. Alternative propellants such as those approved for food use by FDA (F-115 and FC-318),[2] although more expensive, and F-22 could be substituted for F-11 and F-12 for such product types. In view of the small volumes of chlorofluorocarbons consumed, their continued use in medicinals and pharmaceuticals should be considered.

Also of economic importance is the cost of converting aerosol filling equipment now using chlorofluorocarbons to alternative propellants or mechanical delivery systems. The cost of converting to alternative fluorocarbons or chlorofluorocarbons that have about the same thermodynamic properties as F-11 and F-12 should be negligible.

Conventional filling lines can also be converted to carbon dioxide pressurizing units with add-on equipment at a cost estimated at $7,000[6] to $50,000 per line.[7] Most industry estimates of the additional equipment cost per line were approximately $10,000. One company which has converted a chlorofluorocarbon filling line to carbon dioxide reports a daily savings of $3,000 because of the lower propellant cost.[8] Thus, the cost of add-on conversion equipment can be rapidly recovered. Conventional fill lines can also be adapted to fill a bladder delivery system at a cost of not more than $10,000.[9]

C. Foam-Blowing Agents

The use of viable substitutes for the chlorofluorocarbon blowing agents in foams, and hence any economic evaluations, is very difficult to assess as delineated earlier in Chapter V. Chlorofluorocarbons impart specific properties or meet specifications that no other known substitute can duplicate, so that any suggestion of viable substitutes and the resultant economic considerations would be based on the assumption that such alternative systems will provide a foam with identical or acceptable properties. In many instances this assumption is, at best, rather tenuous.

In very general terms, if all 78 million pounds of the current chlorofluorocarbons used in foams were eventually replaced by alternative blowing agents costing three times the current blowing agent price, the overall increased cost would total $62 million. At the current annual output of 898 million pounds of chlorofluorocarbon-blown foams, the added cost to the user would be about $0.065/lb. For a typical flexible foam, this would amount to an approximate 16% price increase. This example is for illustrative purposes only as no single material is known that could serve as an across-the-board replacement for chlorofluorocarbons. The principal utility of this example is to place emphasis on the fact that the cost of the blowing agent represents a minor factor with respect to total raw material cost.

In 1974, approximately 45% of all flexible urethane foam and about 88% of all rigid urethane foam utilized chlorofluorocarbons as blowing agents. These two applications accounted for 90% of the total utilization of chlorofluorocarbons as blowing agents.

In flexible urethane foams, carbon dioxide and methylene chloride can be substituted as blowing agents in many noncritical applications. For carbon dioxide-blown foams, the cost of the foam would show an approximate 15% increase in cost due to the necessity for increased isocyanate consumption in the foam developing process. As discussed earlier in Chapter V, Dow Chemical Company has stated that flexible urethane slab foams can be prepared, using methylene chloride as a blowing agent, with approximately the same foam properties as produced with F-11. The cost of the methylene chloride blowing agent is approximately one-half that of F-11 and the resultant foam cost, based on raw materials, is $0.365/lb as opposed to $0.372/lb for the chlorofluorocarbon-blown foam. Urethane grade methylene chloride from other suppliers would likely produce similar results. The use of other blowing agents for flexible foams has not been developed to a sufficient state of technology to predict their successful application and, hence, the quantity of blowing agent necessary to produce an acceptable foam. If it is assumed that the concentration of these materials would be approximately the same as the current blowing agents, then the cost differential would be expected to be very small since, at current prices, the F-11 blowing agent represents only about 4% of the total raw material cost. If the use of substitute blowing agents led to an increase in the consumption of isocyanate, then the final cost of the foam would show a marked increase in cost per pound.

In rigid urethane foams, the chlorofluorocarbons are considered essential in achieving the low thermal conductivity required for insulating foams. While a few other materials (mostly chlorocarbons) are known that compare with the low thermal conductivity of the present blowing agents, these materials are not currently used in the preparation of insulating foams and it is not known if they could produce a foam with acceptable physical characteristics. It is possible that compounds, other than the chlorofluorocarbons now used almost exclusively for insulating foams, could be developed for use as auxiliary blowing agents; however, to date no satisfactory substitute has been found.

D. Degreasing and Dry Cleaning

In 1975, an estimated 60 to 68 million pounds of F-11, F-113 and F-113 blends and azeotropes were used in cleaning and drying applications, including dry cleaning. Using an average weight of 11.6 lb/gal, calculated from F-113 and six of the common blends and azeotropes, this represents approximately 5.2 to 5.9 million gallons of solvent. Current suggested retail price data, based on tankcar quantities (30,000 lb), are presented below for suitable chlorocarbons, F-113, and the six blends or azeotropes. In this listing, the F-113 mixtures are products of E. I. du Pont de Nemours and Company, Inc. Similar products produced by other manufacturers, such as Allied Chemical, would be competitively priced with those shown in the list. The composition of each of these blends or azeotropes was stated previously in Section VI.

Product	Price per Gallon
1,1,1-Trichloroethane	$2.12
Trichloroethylene	2.155
Methylene chloride	1.95
Perchloroethylene	2.22
Alkaline cleaners	2.00
F-113 (100%)	6.53
TMC	4.80
TA	5.69
TE	6.28
T-E 35	4.73
T-WD 602	6.30
T-P 35	4.66

Since a compilation of the total quantity of each of the F-113 products consumed was not available, an average price of $5.57/gal was used to calculate a current market of $29 to $33 million in 1975. The possible chlorocarbon and alkaline cleaner substitutes show an average price of $2.09/gal, and have a market value of $10.9 to $12.3 million. The market differential would be approximately $18 to $21 million.

For those applications in which chlorocarbons may be considered as substitutes, however, additional costs would likely be incurred. Due to their higher toxicity, vapor-control systems may be required. It has been stated in the Arthur D. Little report[17] that vapor-control systems may initially cost from $50 to $9,000 per degreasing unit, depending upon the specific system, with yearly operating costs in the range of $150 to $400/unit. However, the vapor-control systems would decrease the amount of solvent loss and result in some cost savings. Aside from vapor-control systems, additional equipment such as solvent baths, spray systems, water baths, or oven dryers may be necessary dependent upon the specific solvent degreasing application. In addition to equipment costs, added costs may be incurred including higher labor costs resulting from multistep cleaning processes instead of the current single step process, higher incidence of incompletely cleaned products which must be returned to the cleaning process, additional solvent cost since most multistep cleaning processes use two or more different solvents, and other costs unique to the specific cleaning application. The total additional costs cannot be realistically estimated since such costs would vary considerably depending upon each specific application.

For dry-cleaning applications, perchloroethylene and petroleum solvents (e.g., 140-F) would be the possible substitute for specialty cleaning applications. While both of these solvents are considerably cheaper in price than the F-113-based "Valclene" solvent, the greater solvent mileage obtained with "Valclene" results in approximately equal costs.[1] Perchloroethylene can be used on leather products only if they have been specially treated in the finishing process. Petroleum solvents, such as 140-F, may be used to clean furs but, as stated in Section VI, these solvents are somewhat restricted with regard to cleaning establishments.

The area of dry-cleaning applications is very small and the use of substitutes would probably have little overall economic effect unless the dry-cleaning establishment was entirely "Valclene"-based. In this case, the economic impact would be dependent upon the financial stability of the individual establishment.

REFERENCES TO SECTION VIII

1. Arthur D. Little, Inc., "Preliminary Economic Impact of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons," EPA Contract No. 68-02-1349, Task 8, Publication No. EPA-450/3-75-073, NTIS No. PB-247-115, September 1975.

2. Title 21, Code of Federal Regulations, 121.1065, 121.1181, and 121.101, Supplied by John E. Thomas, Assistant to the Director, Division of Regulatory Guidance, Bureau of Foods, Food and Drug Administration.

3. Howard, D. K., P. R. Durkin, and A. Hanchett, "Environmental Hazard Assessment of One and Two Carbon Fluorocarbons," EPA Contract No. 68-01-2202, Technical Report No. TR-74-572, EPA Report No. 560/2-75-003, NTIS No. PB-247-419 (1974).

4. Personal communication with the American Can Company, Shawnee Mission, Kansas, November 1975.

5. Modern Packaging Encyclopedia and Planning Guide, Vol. 47, No. 12, December 1974.

6. Personal communication with Mr. Charles S. Hayes, Applications Engineer, Chemetron Corporation, Chicago, Illinois, September 1975.

7. Confidential communication with industry source, September 1975.

8. "An Aerosol Filler's Experience with CO_2 as a Propellant," Soap/Cosmetics/Chemical Specialties, pp. 94 to 96, October 1975.

9. Confidential communication with industry source, September 1975.

APPENDIX A

CHLOROFLUOROCARBON MANUFACTURING PROCESSES

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Any significant reduction in the production of fluorocarbons* will have an impact on the employment and sales of producers of the fluorocarbons and their principal precursors. The precursors are shown diagrammatically in Figure A-1. The chemical reactions behind this diagram are listed in Table A-1. The precursors considered in this analysis are hydrofluoric acid used in the production of all fluorocarbons; carbon tetrachloride used in the production of F-11, F-12 and F-13; and carbon disulfide used to produce some of the carbon tetrachloride. The rest of the carbon tetrachloride is produced as a co-product with perchloroethylene by the chlorination of propylene. Chloroform is produced by the chlorination of methanol. Chloroform is also considered in this analysis, as it is used to make F-22, which is assumed to be a permissible substitute for F-11 and F-12 in refrigeration. Perchloroethylene, from which F-113 and F-114 are produced, is not included in this analysis because fluorocarbons consume only about 8%[1/] of the perchloroethylene production.

Fluorspar, from which hydrofluoric acid is produced, is also excluded from this analysis because most of the fluorspar consumed in the United States is imported (97%), primarily from Mexico. Fluorspar currently carries a high import duty, while hydrofluoric acid carries none. As a result, any new facilities built to produce hydrofluoric acid for U.S. consumption will probably be built outside of the U.S. to avoid the tariff.[2/] A tariff adjustment might be considered as part of a package to ameliorate the impacts of reduction in fluorocarbon production.

Capacity, production, and employment estimates for fluorocarbons and their principal precursors are presented in Table A-2. These figures do not include the new Du Pont "Kel-chlor" facility currently in operation in Corpus Christi, Texas. Du Pont's plans show the completed facility rated at 500 million pounds of fluorocarbons annually, which represents almost a 50% increase over present U.S. capacity.

In 1973, about $275 million worth of fluorocarbons were produced in the U.S. This figure includes F-11, F-12, F-13, F-21, F-22, and F-113 and F-114. Direct and indirect employment supported by fluorocarbon production has been estimated at about 6,200 (see Table A-2). Carbon disulfide production comes under SIC-2869, Industrial Organic Chemicals (2869 is the SIC for fluorocarbons and chlorocarbons as well). The 1972 Census of Manufacturers shows about $90,000 of product produced in that year for each employee in SIC-2869. On the basis of figures, fluorocarbon-related employment in carbon-disulfide production can be estimated at about 100.

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* In this section, the term fluorocarbon is intended to denote chlorofluorocarbons.

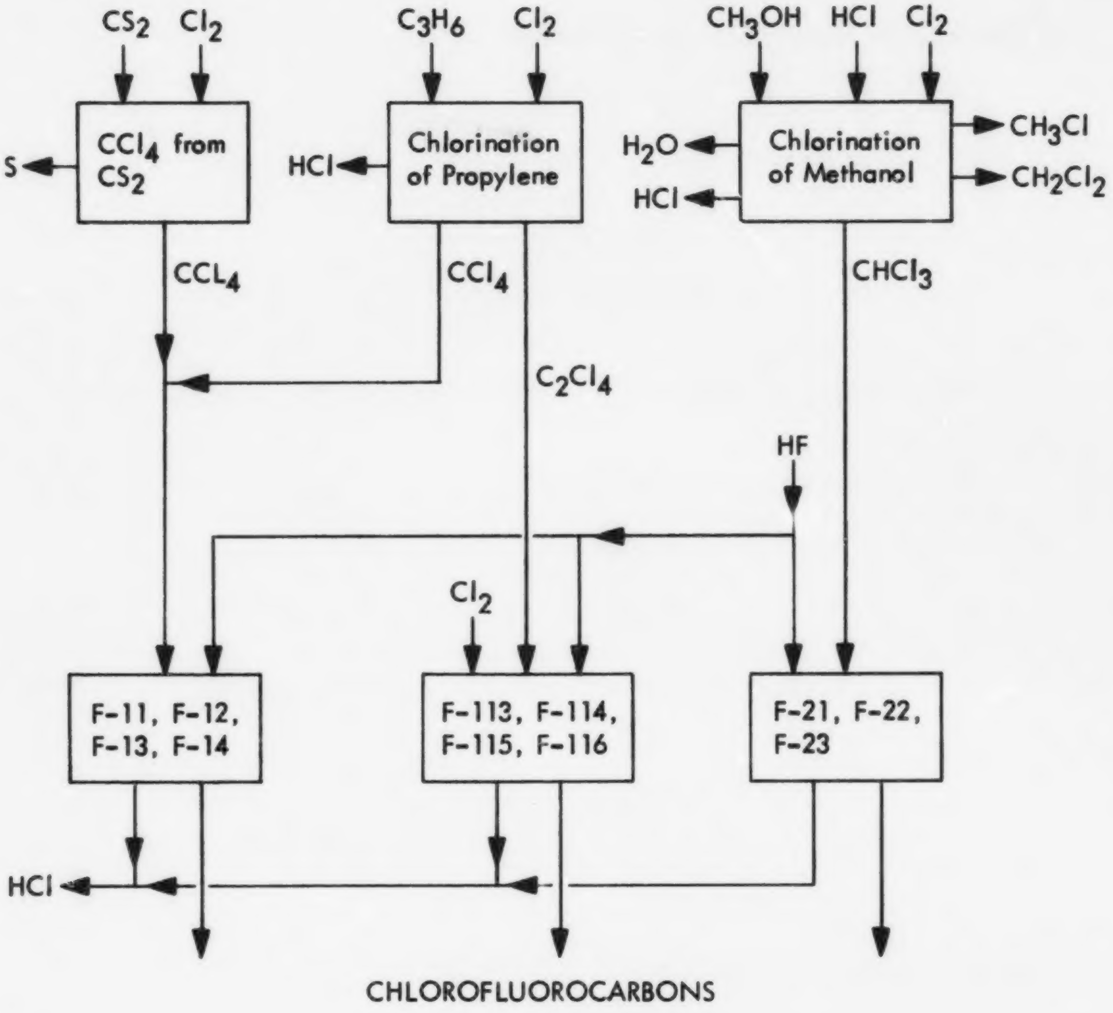
CS_2
Cl_2
CCl_4 from CS_2
S
C_3H_6
Cl_2
Chlorination of Propylene
HCl
CH_3OH
HCl
Cl_2
Chlorination of Methanol
H_2O
HCl
CH_3Cl
CH_2Cl_2
CCL_4
CCl_4
C_2Cl_4
$CHCl_3$
HF
Cl_2
F-11, F-12, F-13, F-14
F-113, F-114, F-115, F-116
F-21, F-22, F-23
HCl
CHLOROFLUOROCARBONS

Figure A-1 - Fluorocarbons and Their Principal Precursors

TABLE A-1

THE CHEMISTRY OF FLUOROCARBONS AND THEIR PRINCIPAL PRECURSORS[a,b/]

Fluorocarbons from Carbon Tetrachloride

$CCl_4 + HF \longrightarrow CCl_3F + HCl$	F-11
$CCl_3F + HF \longrightarrow CCl_2F_2 + HCl$	F-12
$CCl_2F_2 + HF \longrightarrow CClF_3 + HCl$	F-13
$CClF_3 + HF \longrightarrow CF_4 + HCl$	F-14

Fluorochlorination of Methane (this method is not used commercially in the U.S.).

$CH_4 + HF + Cl_2 \longrightarrow CHCl_2F$	F-21
$+ CHClF_2$	F-22
$+ CHF_3$	F-23
$+ CCl_3F$	F-11
$+ CCl_2F_2$	F-12
$+ CClF_3$	F-13
$+ CF_4 + HCl$	F-14

Fluorocarbons from Chloroform

$CHCl_3 + HF \longrightarrow CHCl_2F + HCl$	F-21
$CHCl_2F + HF \longrightarrow CHClF_2 + HCl$	F-22
$CHCl_2F + HF \longrightarrow CHF_3 + HCl$	F-23

TABLE A-1 (Continued)

Fluorocarbons from Perchloroethylene

$C_2Cl_4 + 3HF + Cl_2 \longrightarrow C_2Cl_3F_3 + 3HCl$ F-113

$C_2Cl_3F_3 + HF \longrightarrow C_2Cl_2F_4 + HCl$ F-114

$C_2Cl_2F_4 + HF \longrightarrow C_2ClF_5 + HCl$ F-115

$C_2ClF_5 + HF \longrightarrow C_2F_6 + HCl$ F-116

Carbon Tetrachloride and Perchloroethylene from Propylene

$C_3H_6 + 7Cl_2 \longrightarrow CCl_4 + C_2Cl_4 + 6HCl$

Chloroform from Methanol

$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$

$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$

$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$

Carbon Tetrachloride from Carbon Disulfide

$CS_2 + 3Cl_2 \xrightarrow[\text{catalyst}]{\text{Fe}} S_2Cl_2 + CCl_4$ Carbon Tetrachloride

$CS_2 + 2S_2Cl_2 \longrightarrow 6S + CCl_4$

Carbon Disulfide

$C + 2S \longrightarrow CS_2$

(in conjunction with carbon tetrachloride production) } carbon disulfide

Or $CH_4 + 4S \longrightarrow CS_2 + 2H_2S$

TABLE A-1 (Concluded)

Hydrofluoric Acid From Fluorspar

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ Hydrofluoric Acid

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a/ The principal precursors described in this table are those with more than 10% of their present U.S. production devoted to fluorocarbon production.

b/ Sources: Noble, H. L., "The Chemical Marketing Research Association Review and Forecast," CMRA Paper No. 766, May 1972.
Faith, W. L., D. B. Keyes, and D. L. Clark, Industrial Chemicals, 3rd ed., John Wiley and Sons, Inc., New York (1965).
Personal communication with chlorofluorocarbon manufacturer.

TABLE A-2

FLUOROCARBON AND FLUOROCARBON RELATED PRODUCTION AND EMPLOYMENT

Product	Million of Pounds Per Year: Capacity[a]	Million of Pounds Per Year: 1973 Production	Million of Pounds Per Year: Quantity Consumed in Fluorocarbon Production	Percent of Production Denoted to Fluorocarbons	1973 Price Per Pound ($)	1973 Dollar Volume of Production (millions)	Estimated Employment[m]	Employment Supporting Fluorocarbon Production
F-11 and F-12	970[b]	834[h]			0.19 (F-11)[h] 0.24 (F-12)	180.7		
F-21 and F-22	160[b]	136[h]			0.45	61.2		
F-113 and F-114	68[b]	58[d]			0.55[n]	31.9		
Subtotal Fluorocarbons	1,198[e]	1,028				273.8	2,100[p]	2,100[p]
Carbon Tetrachloride								
From CS_2	650[f]	353[g]						
From Chlorination of Methane	928	694						
Total	1,578[e]	1,047[h]	1,047	99.9[i]	0.06	62.8	611	611[q]
Chloroform from Chlorination of Methane	293[e]	253[d]	205	81.0[c]	0.07	17.7	172	139[q]
Carbon Disulfide	850[e]	775[j]	194	25.0[l]	0.05[o]	38.8	431[m]	108
Hydrofluoric Acid	814[e]	731[k]	305[k]	41.6		135.4[l]	800[k]	330[k]
Subtotal for Principal Precursors						254.7	2,014	1,188
Total								3,288
Indirect Employment[o]								2,897
Direct and Indirect Employment Supported by Fluorocarbon Production[o]								6,185

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[a] Capacity does not include Du Pont's new Kel-chlor facility under construction in Corpus Christi, Texas. Preliminary plans show the eventual capacity of this plant to be 500 million pounds of F-11, F-12, F-13, F-21, and F-22 annually.

[b] MRI estimate based on c/, d/, and e/

[c] ADL Table V-8.

[d] ADL Table V-6.

[e] SRI 1975 Directory of Chemical Producers.

[f] Figures from e/; includes some produced by chlorination of methane.

[g] 1972 production estimated from the CS_2 production at 1,100 lb of CS_2 producers 1 ton of CCl_4. W. L. Faith, Donald B. Keyes, and Ronald L. Clark (1965), Industrial Chemicals, Third Edition, p. 229.

[h] U.S. International Trade Commission (1975), U.S. Production and Sales of Miscellaneous Chemicals for 1973.

[i] Ninety-five percent of carbon tetrachloride is used to produce F-11 and F-12. Essentially all of the remaining 5% is converted to perchloroethylene by pyrolysis and used to make F-113 and F-114.

[j] 1972 production from the Chemical Marketing Reporter, July 24, 1972.

[k] ADL Table V-13.

[l] ADL Table V-12.

[m] Employment estimate based on $90,000 of product per employee per year. This figure was derived from the 1972 Census of Manufacturers for SIC 2869, Industrial Organic Chemicals.

[n] MRI estimate based on current prices.

[o] Obtained from "direct employment supporting fluorocarbon production," using a multiplier of 1.881 derived from the U.S. Department of Commerce (1968) Input-Output Structure of the U.S. Economy: 1967 for industry classification 27.01 Industrial Organic and Inorganic Chemicals.

[p] ADL Table I-5.

[q] Estimate based on p/.

But this employment generates additional activity in the rest of the economy. The Input-Output Structure of the U.S. Economy: 1967 (published in 1974 by the U.S. Department of Commerce) measures these indirect effects in 367 different industry categories. The numbers in these tables for industry classification 27.01, Industrial Organic and Inorganic Chemicals, indicate that each job in organic and inorganic chemicals supports about 0.881 job in other segments of the economy, or that roughly 2,900 jobs altogether are supported by fluorocarbon production. Many of these jobs will be located near the facilities which produce fluorocarbons and their principal precursors.

These calculations indicate that approximately 6,200 people in the U.S. today are employed directly or indirectly by the production of fluorocarbons. This analysis is based on 1973 information, when about 1 billion pounds of fluorocarbons were produced.

A small change in production would probably have no identifiable impacts on employment in the industry. On the other hand, if no fluorocarbons were made next year, employment would be seriously affected. Any significant reduction in fluorocarbon production will create an economic impact somewhere in between these two extremes. Assuming that the reduction in fluorocarbon production is significant, alternative employment will be needed for three chemical workers for each million pounds of fluorocarbons no longer produced. If alternative employment is not found for these chemical workers, an additional three jobs in other segments of the economy will be affected for each million-pound reduction.

The companies producing both fluorocarbons and their principal precursors are listed in Table A-3. It was assumed for the purposes of this study that F-22 would be an allowable alternative to F-11 and F-12 in refrigeration. F-22 is made from chloroform, while F-11 and F-12 are made from carbon tetrachloride. Chloroform and carbon tetrachloride are co-products in the chlorination of methane. However, only a small percentage of the production of chloroform is manufactured in this manner because the freedom to adjust the ratio of the final products is limited. Most chloroform is co-produced with methylene chloride by the chlorination of methanol. This process allows more freedom in adjusting the ratio of the final products according to market demand. Those facilities producing carbon tetrachloride from carbon disulfide cannot make this adjustment. However, the facilities producing carbon disulfide will not be as seriously affected, since the production of carbon tetrachloride accounts for only 25% of the utilization of carbon disulfide.

The locations of the facilities producing fluorocarbons and their principal precursors and details on population and employment in each of these areas are shown in Table A-4. Because of economic considerations, some of these production facilities will close as a result of any sizable reduction in fluorocarbon production.

TABLE A-3

COMPANIES PRODUCING FLUOROCARBONS AND THEIR PRINCIPAL PRECURSORS

Company	Fluorocarbons	Chloroform	Carbon Tetrachloride from Chlorination of Methane	Carbon Tetrachloride from Carbon Disulfide	Carbon Tetrachloride Total	Carbon Disulfide	Hydrofluoric Acid
Allied Chemicals	310	30	8		8		224
Alcoa							110
Diamond Shamrock		18					
Dow		130	275		275		
Du Pont	500[a]		500[b]				200
Essex Chemicals							22
FMC				300[c]	300	180	
Kaiser Aluminum and Chemicals	50						100
Kewanee Oil							36
Lehigh Valley Chemicals							10
Olin							26
Pennwalt	115					10	50
PPG						60	
Racon	20						
Stauffer		75	70	350	420	600	36
Union Carbide	200						
Vulcan	—	40	75	—	75	—	—
Total	1,195	293	928	650	1,078	850	814

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[a] Does not include the new Kel-chlor facility under construction in Corpus Christi, Texas, which is designed for another 500 million pounds per year.

[b] Includes carbon tetrachloride and chloroform.

[c] FMC produces some carbon tetrachloride from carbon disulfide and some from chlorination of methane.

Source: SRI 1975 Directory of Chemical Producers.

TABLE A-4

LOCATION OF PRODUCTION FACILITIES FOR FLUOROCARBONS AND THEIR PRINCIPAL PRECURSORS

			Population		Employment		
			1970	% Change 1960-1970	1970	% Change 1960-1970	Related Firm
	Alabama						
1.	Le Moyne	Mobile SMSA	376,690	3.7	93,178	-12.3	Stauffer
	California						
2.	El Segundo	Los Angeles/Long Beach SMSA	7,040,697	16.6	2,826,565	8.1	Allied
3.	Antioch Pittsburgh	San Francisco/Oakland SMSA	3,108,026	17.3	1,267,643	17.8	DuPont Allied/Dow
	Delaware						
4.	Delaware City North Claymont	Wilmington, Delaware/ New Jersey/Maryland, SMSA	499,493	20.5	192,061	39.9	Stauffer Allied
	Illinois						
5.	Joliet	Chicago SMSA	6,977,611	12.2	2,852,017	13.6	Olin
	Danville	Vermilion County	42,570	1.7	16,856	5.4	Allied
	Indiana						
7.	East Chicago	Chicago SMSA	6,977,611	12.2	2,852,017	13.6	DuPont
	Kansas						
8.	Wichita	Wichita SMSA	389,352	2.0	149,169	18.0	Racon/Vulcan
	Kentucky						
9.	Louisville	Louisville SMSA	826,553	14.0	321,180	25.7	DuPont/Stauffer
10.	Calvert City	Marshall County	20,381[a]	21.8[a]	7,143[a]	40.6	Pennwalt
	Louisiana						
11.	Baton Rouge	Baton Rouge SMSA	285,167	24.0	102,577	30.6	Allied
12.	Geismar	Ascension County	37,086[a]	32.8[a]	10,805[a]	45.4	Allied/Vulcan
13.	Gramercy	St. James County	19,733[a]	7.4	4,976[a]	15.3	Kaiser
14.	Plaquemine	Iberville County	30,746[a]	2.7[a]	8,018[a]	3.1	Dow

TABLE A-4 (Concluded)

			Population		Employment		
			1970	% Change 1960-1970	1970	% Change 1960-1970	Related Firm
	Michigan						
15.	Montague	Muskegon/Muskegon Heights SMSA	157,426	5.0	56,081	63.2	DuPont
	New Jersey						
16.	Elizabeth Newark	Newark SMSA	1,859,096	10.0	762,303	12.0	Allied
17.	Paulsboro Thorofare	Philadelphia, Pennsylvania, New Jersey SMSA					Vulcan Essex
18.	Deep Water - Salem County		60,346a/	2.8a/	23,203a/	7.9	Pennwalt DuPont
	New York						
19.	Niagara Falls - Buffalo SMSA		1,349,211	3.2	509,789	7.0	Stauffer
	Ohio						
20.	Ceveland - Ceveland SMSA		1,349,211	3.2	828,585	19.7	Kewanee Oil
	Pennsylvania						
21.	Glendon	Philadelphia, Pennsylvania New Jersey SMSA	4,822,245	11.0	1,878,497	14.2	Lehigh Valley Chemical
	Texas						
22.	Corpus Christi	Corpus Christi SMSA	284,832	6.8	96,252	38.7	DuPont
23	Greens Bayou La Porte	Houston SMSA	1,985,031	40.0	797,421	69.5	Pennwalt/Stauffer
24.	Freeport - Brazoria County		11,997	3.3	4,826	9.0	DuPont Dow
25.	Point Comfort - Calhoun County		17,831a/	7.5a/	5,835a/	13.3	Alcoa
	West Virginia						
26.	Belle Nitro South Charleston So. Charleston - Institute	Charleston SMSA	229,515	-9.3	82,127	-1.0	Diamond Shamrock Allied FMC Union Carbide
27.	Moundsville - Marshall County		13,560	-10.6	4,896	7.8	Allied
28.	Natrium - Marshall County		37,598a/	-1.2a/	13,224a/	15.0	Pittsburgh Plate Glass

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a/ County data.

Source: United States Census of Population, 1960 and 1970, General Population Characteristics, General Social and Econ. Characteristics.

APPENDIX B

THE ROVAC AUTOMOTIVE AIR CONDITIONING SYSTEM

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SOCIETY OF AUTOMOTIVE ENGINEERS, INC.
400 Commonwealth Drive, Warrendale, Pa. 15096

The Rovac Automotive Air Conditioning System

Thomas C. Edwards
The Rovac Corp.

SOCIETY OF AUTOMOTIVE ENGINEERS

Automotive Engineering Congress and Exposition
Detroit, Michigan
February 24-28, 1975

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THE VAST MAJORITY of conventional refrigeration and air conditioning systems in use today embody the well known and highly developed reversed Rankine (vapor compression) cycle. Of much lesser use is the reversed Brayton or "dense air" cycle. Until recently, the air cycle has been shown to be of value only in restricted uses such as the thermal management of turbine-powered aircraft.

The vapor compression cycle operates on the principle of working fluid phase change to approximate isothermal heat transfer at the source and sink conditions in order to approach the reversed Carnot efficiency. The ideal reverse Brayton cycle, on the other hand, does not have the thermodynamic benefit of working fluid phase change. However, investigations of the rotary vane air cycle system performed by the author, as well as the activities of other investigators, have verified that the air cycle system, when employed with proper hardware and accounting for properly natural moisture phase-change effects, can produce exceptional performance.

The earliest development work (1)* verified that the internal thermodynamic performance of the rotary vane air cycle system was quite promising, but that the system at that time was harnessed by extremely low mechanical efficiency rotary vane hardware. Thus, thermodynamic achievability of the rotary vane air cycle system was proven, but the serious mechanical constraint in the form of mechanical friction was also fully exposed. Continued development efforts, however, have yielded effective means of increasing the mechanical efficiency of rotary vane air cycle hardware, and therefore has permitted greatly increased total performance.

As is well known in the design of rotary sliding vane hardware, the most serious source of mechanical friction lies at the interface of the vane tip and the stator housing. (2) Not only does this tip friction vector induce a direct rubbing me-

ABSTRACT

The ROVAC air conditioning system, a new system that employs air as the refrigerant, is a combination rotary compressor/expander unit. A prototype has been modeled, designed, fabricated, laboratory tested, and field tested in a full size four door 1973 Dodge Coronet. The description of the new system, the analysis, design and actual test results are reported here.

The objective of the engineering program was to demonstrate and prove the capability of the ROVAC system to effectively and efficiently air condition automobiles. The prototype system installed in the Dodge Coronet produces delivered cooling capacity on the order of one to one and a half tons per thousand rpm and has produced delivered coefficients of performance at relatively high humidity levels (150-180 grains water per pound of dry air) rivaling the best developed conventional vapor compression air conditioning systems.

While the present system reported herein has not reached the levels of performance predicted by detailed computer models, continued hardware improvement is facilitating actual performance very near the levels predicted to be practically achievable.

During actual in-car jury tests, the prototype ROVAC air conditioning system brings the average passenger compartment temperature from a thermally soaked condition of 107°F down to 72°F in less than two min with five passengers at an average road speed of 30 mph.

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*Numbers in parentheses designate References at end of paper.

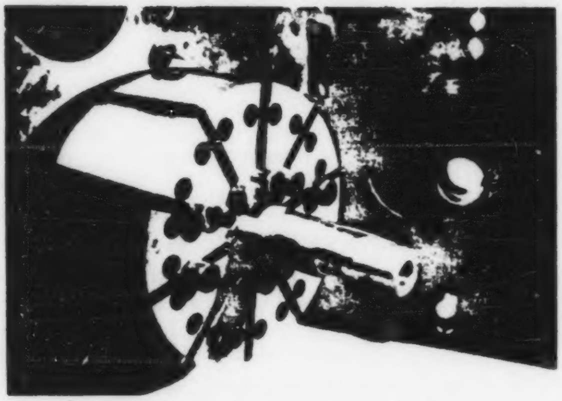

Fig. 1 - First generation cam-guided circulator

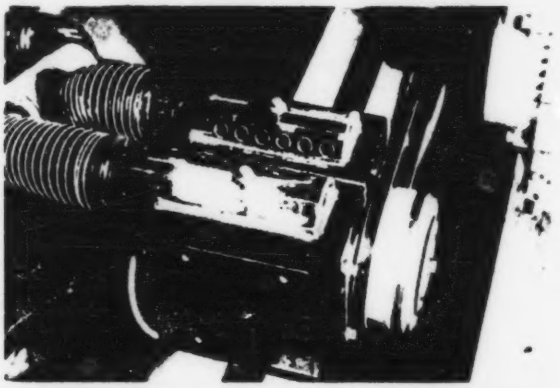

Fig. 2 - First cam-guided machine in operation – note formation of ice crystals in outp..t manifold

chanical loss, but it also increases the "cocking" of the vane inside the rotor slot. This serves to further intensify frictional losses between the vane sides and the rotor slots.

Various approaches to eliminating the vane tip friction vector were considered; the embodiment that presented the best promise for sliding vane machines involves cam-guided vanes wherein the kinematics of the vanes are dictated entirely by end-plate cam paths that engage in a rolling element fashion, small solid protrusions from the vanes. Within this concept, since the vane motion is dictated entirely by the cam profile (independent of the stator profile), the rotating assembly and cam profile can be designed such that the vane tip just clears the stator wall during operation. This, of course, eliminates all tip friction and wear, and thereby greatly increases the mechanical efficiency and longevity of the unit. This concept was transformed into hardware and is pictured as first embodied in Fig. 1.

As shown in Fig. 1, the cam path is of the double-acting type with small needle-bearing mounted polyamide rollers fitted to the vanes. While this particular unit did not meet the specified design tolerances, it did demonstrate the basic mechanical fesibility of the concept and did produce a COP in the vicinity of 1.0, almost twice the original Purdue machine. Fig. 2 shows this unit in operation. Since the fabrication and test of this first cam-guided machine, a considerable amount of activity has been dedicated to analysis, design, and fabrication of more sophisticated machines.

Preliminary analytical results involving predictions of actual mechanical efficiency of rotary cam vane machines indicated that mechanical efficiencies for both the compressor and expander sides could approach or exceed 90%. (This would indicate a total mechanical efficiency for the air cycle machine would be greater than 80%.) Subsequent in-depth detailed computer-aided analyses recently performed by a United States Air Force contractor (3) has predicted that even greater mechanical efficiencies can be achieved with real machines. Namely, compressor and expander mechanical efficiencies on the order of 95% are predicted with Coulomb coefficients of friction of 0.1-0.05. Reasons for the somewhat higher predicted mechanical efficiency than might have been expected are apparently couched in the following facts:

1. Very little mechanical motion takes place for a large change in volume. (For example, the compression or expansion process takes place in approximately one-tenth of a revolution.)
2. At operating speeds, the vanes appear to float or oscillate azimuthally within the rotor slot (apparently due to the absence of the vane tip friction vector and the pressure-opposing Coriolis acceleration component).

This last consideration is lending explanation to the very small vane wear that has been observed in the various tests performed on the first cam-guided machine (Fig. 2) which has logged in excess of 300 h and displayed maximum vane side wear of 0.0003 in during this time.

The obvious item that must be considered when appraising this type of rotary vane machine is that of leakage. The importance of this consideration has been borne out during the development of ROVAC air cycle machines. It can be easily shown, for example, that vane tip to stator clearances exceeding approximately 0.001 in will seriously inhibit the total performance of the air cycle system at low rotor speed due to the relatively long residence times of a given charge of air within a vane segment. This problem received considerable attention in design and fabrication, and was ultimately overcome through refined rotating component design and enhanced non-rotating component fabrication techniques.

Upon verification of both the thermodynamic fesibility and the mechanical operability of the cam vane machines, it became apparent that ROVAC air cycle systems definitely had the potential of being developed into numerous highly competitive air conditioning and refrigeration products. However, since that realization, another significant discovery was made regarding the basic actual thermodynamic processes upon which ROVAC hardware operate. This discovery and its ramifications are discussed briefly in a subsequent section. First, however, a brief review of the classical reversed Brayton cycle is presented.

THE REVERSED BRAYTON CYCLE

The well-known conventional reversed Brayton cycle employs a single phase working fluid that undergoes four basic

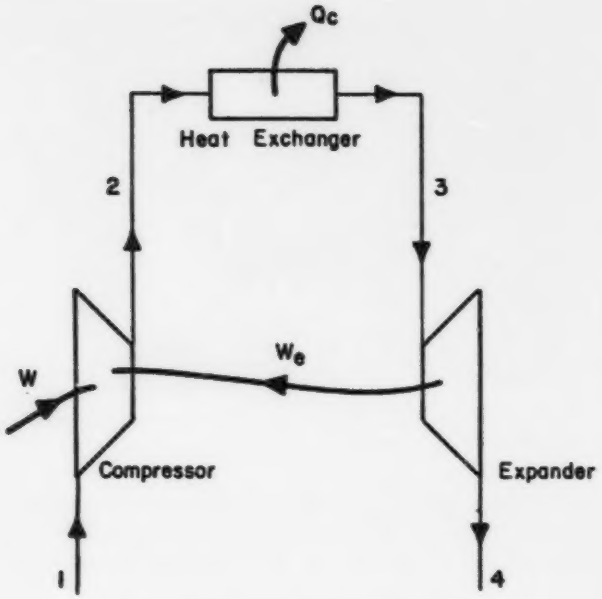

Fig. 3 - Open reversed Brayton cycle system

processes: 1. compression, 2. heat rejection, 3. expansion, and 4. heat acceptance. In the open-cycle form, the heat acceptance process occurs via cold mixing of the working fluid which the ambient gas (usually air) and in the closed-cycle form, heat is accepted through a heat exchanger. Fig. 3 schematically presents the open-cycle form of the reversed Brayton cycle.

As depicted in this figure, ambient air is drawn into the compressor, compressed, pumped into a heat exchanger (intercooler), pumped into the expander, expanded, and finally emerges in a greatly cooled state. For the reversed Brayton cycle, the coefficient of performance (COP), defined as the cooling obtained divided by the energy provided, appears as:

$$\mathrm{COP} = \frac{\dot{Q}L}{\dot{E}_{comp} - \dot{E}_{exp}} \qquad (1)$$

where:

$\dot{Q}L$ = cooling capacity
$\dot{E}_{comp}$ = power provided to compressor
$\dot{E}_{exp}$ = power provided to expander

Under ideal conditions, with polytropic perfect gas behavior, the cooling capacity of the system shown in Fig. 3 can be represented as:

$$\dot{Q}L = \dot{M}\,C_p\left[1 - \left(\frac{1}{r}\right)^{n-1}\right] \qquad (2)$$

and the COP can be represented as:

$$\mathrm{COP} = (r^{n-1} - 1)^{-1} \qquad (3)$$

where:

n = the polytropic process index
r = volume ratio
$\dot{M}$ = mass flow rate
C_p = specific heat at constant pressure

Study of these equations does provide considerable insight into the ideal reversed Brayton cycle. However, when the numerous real effects such as leakage, heat transfer, various pressure losses, and other real effects are considered, the analysis becomes considerably more involved. For a discussion of these matters, the reader is referred to References 1, 2, and 3.

The previous detailed analysis performed by the author contained one significant assumption, that, when considered more carefully, has proven to hold a key to a new thermodynamic cycle. Namely, it was assumed in previous analyses, that atmospheric moisture naturally existing in the inlet air, would not, due to the rapid process rates involved, condense during expansion. Actual experimental data has proven this to be an invalid assumption and further analysis has disclosed that, properly employed, the actual process can greatly improve the operation of ROVAC systems. Before proceeding to this and other new thermodynamic considerations, however, consider the following qualitative description of the system to see how it achieves the processes required to achieve cooling.

THE ROVAC SYSTEM

Fig. 4 illustrates in a generalized fashion the substance of the ROVAC system. In the open cycle form, the system consists of three basic components:

1. Input-Output Duct.
2. Rotary Vane Combination Compression-Expander-Circulator.
3. Heat Exchanger.

The input-output duct serves to provide a path for both the incoming flow of warm air and outgoing cold air. This ducting system is equipped with various processing media such as filters, sound control, or moisture separation means, depending upon the actual application of the particular system.

The circulator unit, which can be considered to be the heart of the system, consists mainly of two items: the stationary portion, termed the stator, and the rotating rotor-vane assembly. The stator housing is also equipped with two endplates which hold the rotor in its axial position and aid in containing the air that circulates through the machine. The rotor-vane assembly consists of a cylindrical rotor equipped with a series of sliding vanes. These vanes are arranged so that they can slide inside the rotor slots as the rotor-vane assembly rotates within the stator, and thereby maintain continuous near-contact with the stator wall.

The heat exchanger, also termed the intercooler, serves to dissipate the heat generated during the operation of the system. This heat exchanger is principally a simple externally finned tube. For some applications, internal finning can also be used to increase the rate of heat transfer.

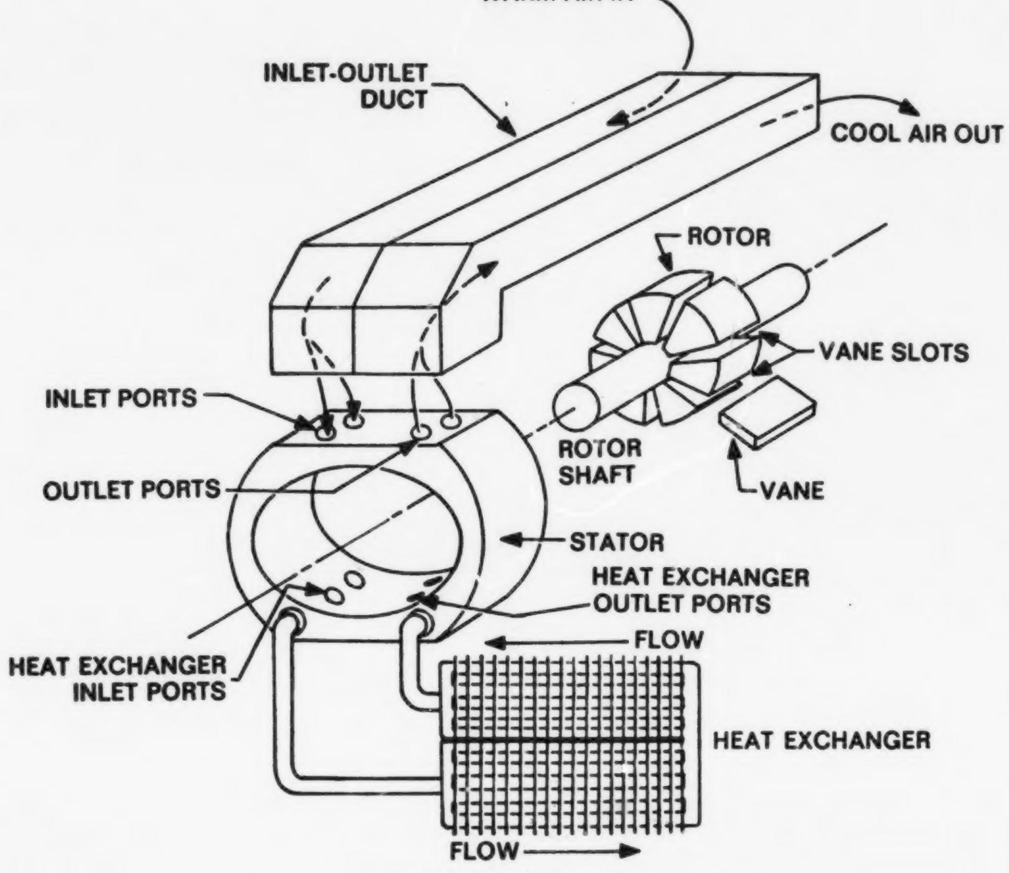

Fig. 4 - Basic ROVAC system

In order to understand how the system functions, consider Fig. 5 which illustrates the system in cross-sectional schematic form. Imagine air (any gas will work, however) entering the system through the input duct at atmospheric pressure and temperature. As the rotor turns counter-clockwise (in this example), air is drawn through the inlet leg of the duct and into the expanding inlet volume V_i. As rotor motion continues, the maximum inlet volume V_1 is filled. The air which is now trapped is then compressed by further rotor rotation to V_2. At V_2 the air has reached an elevated pressure and temperature. The air is then pumped through the heat exchanger, and it cools to a temperature near that of the surroundings, thus transferring heat to the surroundings. (When the system is being employed as a heat pump, the heat exchanger warmth is transferred to the area being heated.) The cooler air then emerges from the heat exchanger (still at an elevated pressure) and enters the expanding volume segment, V_4. Finally, this air is expanded back to atmospheric pressure at V_5 by continued rotor motion. During this expansion process, a large fraction of the work of compression is recovered, thereby greatly reducing the air temperature. Continued rotor rotation then forces the cold air through the output ports and down the output leg of the duct. When the ROVAC system is being employed as an air conditioner or refrigerator, this cold air is circulated to the area being cooled.

THE EFFECTS OF MOISTURE

Early experience with experimental ROVAC systems disclosed that the actual physics and thermodynamics of the air-water mixture was not well understood by the author. Even at the time of this paper, some details of the process are not fully comprehended. To begin the discussion of the effect of moisture, consider on a qualitative basis what happens to the natural ambient moisture as it flows through the cycle. Assume, for example, that the inlet humidity ratio is 100 grains of water per pound of dry air. (Corresponding, for example, to an inlet temperature of, say, 95°F, 40% relative humidity.) During the compression process, the mixture of air and water vapor can generally be considered to become even more superheated because of the higher temperatures occuring during compression. (The higher pressures, of course, tend to lower the superheat. However, the effect of temperature is dominant. Whether superheat or saturation occurs, of course, depends upon the actual compression process path.)

During the intercooling process, the pressure loss is quite

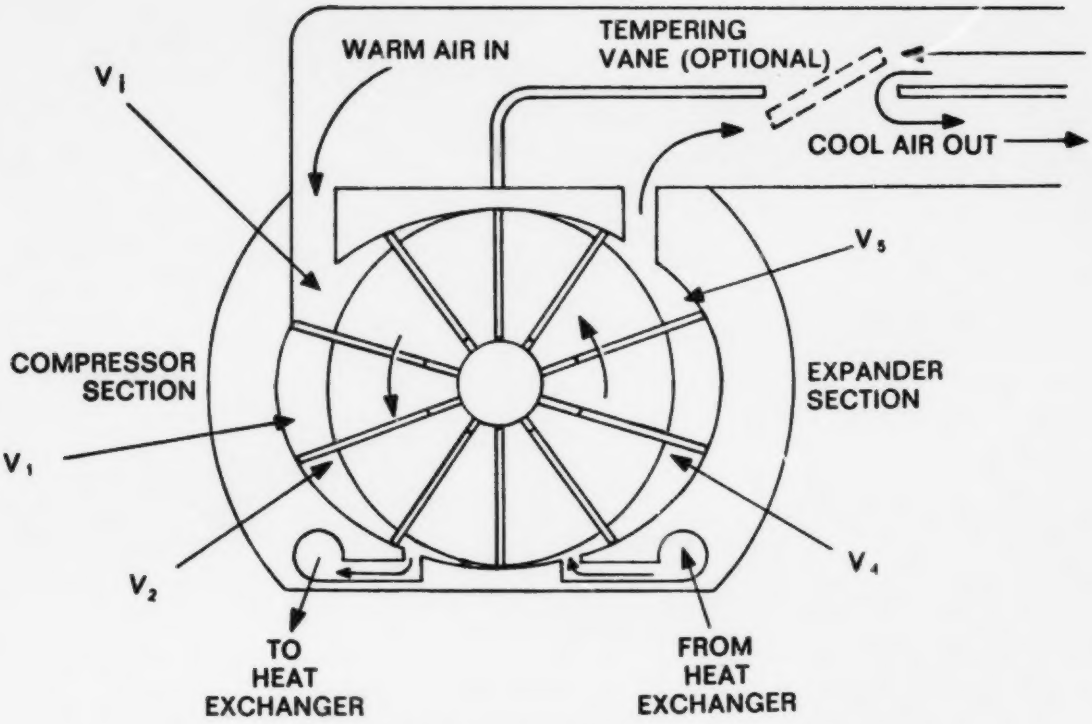

Fig. 5 - Generalized schematic end-view of the ROVAC system

small, (actual systems exhibit only about 0.3-0.75 psi drop) but the temperature drops quite significantly; very near to ambient temperature. Now depending upon actual conditions, part of the condensation occurs inside the intercooler because the relative humidity towards the low temperature side of the heat exchanger will generally attempt to exceed 100%. (Under usual operating conditions, for example, approximately 30 grains of water would be condensed per pound of dry air flowing through the intercooler.)

Next consider what occurs as the saturated moist air enters the expander and expands back down to atmospheric pressure. As expansion begins, both the pressure and temperature of the mixture begins to drop. Since again the temperature drop is thermodynamically more significant as far as the moisture is concerned, the moisture begins to condense further. When this occurs, the energy associated with the condensing water is transferred to the surrounding air. This energy extracted from the vapor, (which caused condensation in the first place) serves to increase the temperature of the air-water mixture. This also, of course, increases its pressure over what it would have been at the same volume with dry air. This means that the expander will have to expand to a larger volume in order to reach the ambient pressure than it would have if no energy was added to the air (remember, of course, that energy was extracted from the moisture and that is why it condensed). This results in a most important event: The recovered expansion work ($\int_{V_4}^{V_5} PdV$) has increased. This effect is portrayed in Fig. 6 where the work process is shown as a polytropic process. (Subsequently, the justification for considering this process to behave in a polytropic fashion will be presented.)

An important additional consequence of the higher energy recovery during expansion is that the final energy state after expansion is lower. Of course, attainment of a low final energy state in the outlet flow is the fundamental goal of the system. One additional important consideration is that through the condensation of moisture at the intercooler, more actual energy is rejected by the system. This results in a yet further reduction in total outlet enthalpy because the expander inlet enthalpy begins at a lower state than the dry air, if one considers the fact that moisture removed is one of the requirements of most air conditioning applications.

The foregoing discussion yields the conclusion that natural moisture is actually an important benefactor for ROVAC systems, in direct contrast to conventional vapor compression units.

THE MIXED MULTI-PHASE POLYTROPIC PROCESS - After some consideration, it was decided that the most expedient approach to modeling the mixed multi-phase expansion process would be to view it as a polytropic. The justification of this assumption is couched in the fact that, insofar as the air is concerned, the process is simply influenced by heat transfer - an effect known to be modeled quite well by the polytropic.

After deciding to model the process as a polytropic, the problem is reduced to finding the correct polytropic index. In the author's approach, the polytropic index of expansion

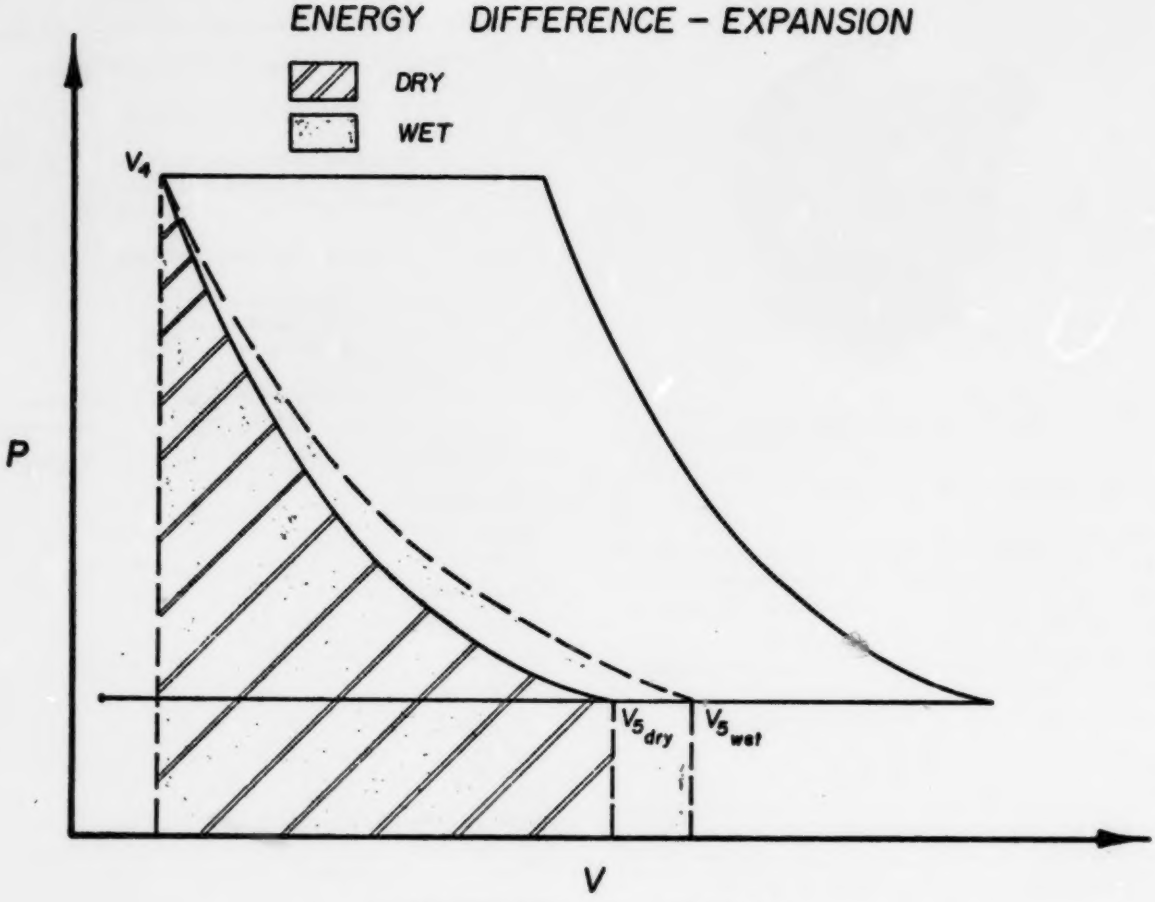

Fig. 6 - Expansion work recovery: wet vs dry air

of wet air is found by considering the amount of work produced during expansion from a consideration of the conservation of energy (first law of thermodynamics: work = Δu) by considering initial and final state point conditions. The same work is then calculated from the quasi-static work integral through the definition of the polytropic index. Since the polytropic index appears in both expressions, it becomes an iterative parameter. That is, using the polytropic index as a parameter, the first law work is matched with the polytropic work. This matching is done in an iterative fashion in a simple computer program until the correct index causes both the work and final state points to match.

Analytical results show that the polytropic index varies only a small amount over an extremely large range in inlet humidity ratio. The reason for this is that the largest reduction in polytropic expansion index is brought about by the amount of water vapor left to condense during expansion. Due to the fact that the normal intercooler operating pressure is in the vicinity of 43-50 psia with an outlet temperature in the range of 80°-100°F, the air can support water vapor content between 52 grains and 70 grains. This relatively small variance in expander inlet vapor content over an extremely large range of inlet humidity ratio confines the polytropic index to the vicinity of 1.24-1.28. This is obviously important because the total power demand of the system will remain constant even though the relative humidity changes markedly. This is also important because the total expander temperature difference will remain approximately constant throughout a large range of ambient humidity. Of course, the delivered cooling capacity will rise significantly with an increase in inlet humidity ratio due to the high pressure moisture condensation. It is thus apparent that the ROVAC air conditioning system exhibits a very favorable characteristic in that the sensible cooling remains approximately constant at all humidity levels. This is, of course, in solid contrast with conventional Freon systems where moisture decreases the sensible cooling delivery.

The approximate properties of the multi-mixed phase thermodynamics were factored into a pre-existing detailed model of the system. Results of the advanced computer program indicated very significant gains in the predicted achievable performance. While the current system test performance falls short of the computer predictions, the actual performance of ROVAC test systems now rivals the performance of high quality factory-installed automotive air conditioning systems. A comparison between predicted and actual performance appears in the following section.

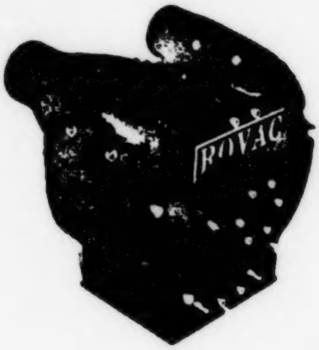

Fig. 7 - Model 308/45/9.5-4 circulator

Table 1 - ROVAC Model 308/45/9.5-4 Performance

Geometry of CIRCULATOR:

Major Axis = 9.50 inches (24.13 cm)
Minor Axis = 6.717 inches (17.06 cm)
Active Rotor Length = 4.0 in (10.16 cm)

Ambient Operating Conditions:

Temperature = 110°F
Pressure = 14.69 psia
Relative Humidity = 57%

	Computer Predicted Performance		Actual Measured Performance	
Parameter	English Units	S.I.	English Units	S.I.
Compressor Outlet				
Temperature	316°F		315°F	
Pressure	47.75 psia		48.2 psia	
Expander Inlet				
Temperature	105.5°F		108°F	
Pressure	47.10 psia		47.5 psia	
Expander Outlet				
Temperature	9°F		34°F	
Pressure	14.65 psia		14.65 psia	
Rotor Speed	1510		1510	
HP Drive	3.875		5.75	
Air Mass Flow Rate	451.0 lbm/h		453 lbm/h	
Cooling Capacity	29,979 BTUH		23,284 BTUH	
COP	3.04		1.59	

ROVAC SYSTEM PERFORMANCE

Based upon design information provided by computer-aided analysis, third and fourth generation anti-friction circulators were designed, fabricated, tested, and partially developed. Fig. 7 shows a photograph of the model 308/45/9.5-4 Circulator (4th generation) and Fig. 8 shows in operation the model 209/45/8-4 machine.

Table 1 presents both predicted and actual data for a typical test of the model 308 machine.

TEST FACILITY AND PROCEDURE - Fig. 9 shows a photograph of the laboratory test facility employed to evaluate the performance of various prototype ROVAC air conditioning systems. The facility consists of a 5 HP DC motor driven by a SCR control and monitoring unit. This prime mover system permits infinitely variable speeds and continuous armature current readout. Due to the properties of the DC driven motor, the delivered torque is linearly proportional to the armature current. Therefore, a knowledge of the armature current permits calculation of the output torque. Since the test facility includes circulator RPM readout, and the drive ratio is known, the input drive horsepower is easily determined.

In addition to power input determination instrumentation, instantaneous heat exchanger inlet and outlet pressures are indicated directly by Heise pressure gages. Ambient relative humidity is provided by an Albion hygrometer. Temperature readout is provided by an Ircon digital copper-constantan thermocouple thermometer. In addition, two channels of transient temperature and pressure measurements are provided through a Hewlett-Packard Model 1704A oscillograph and copper-constantan thermocouple probes. Sound level measuring equipment in the form of a Triplett Model 370 sound

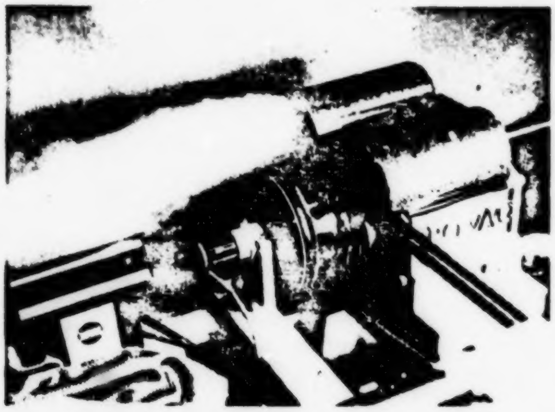

Fig. 8 - Model 209/45/8-4 circulator in operation

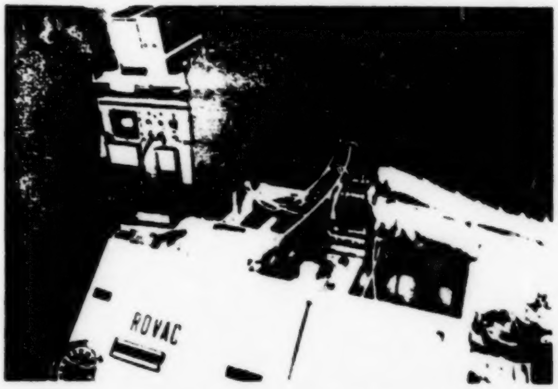

Fig. 9 - ROVAC system test facility

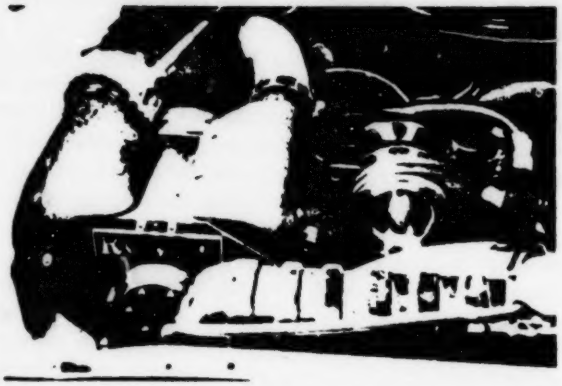

Fig. 10 - ROVAC-Dodge installation

level meter permits measurement of the noise level produced by the system. Mass flow rate is measured by conventional pitot-static methods as well as a Roots type positive displacement flow meter. (Flow tests, however, have proven that the circulator mass flow volumetric efficiency is between 98-99%.)

The chamber which houses the test facility is equipped with an electric heater, humidifier, and air conditioner. Prior to the test, the chamber conditions are set through the use of these items. When the desired chamber conditions are reached and recorded, the test is begun.

Testing the unit is accomplished by simply bringing the rotor speed to the desired level and recording the data indicated by the instrumentation. Immediately after the test, various internal and external surface temperatures are measured and recorded with a special miniature thermocouple probe. The test unit is often then disassembled for visual and metrological inspections.

DISCUSSION OF PERFORMANCE - From Table 1, several conclusions are immediately apparent. For example, the actual delivered COP of each unit rivals the COP of well developed Freon automotive air conditioning system which are reported to produce delivered-to-car COP's on the order of 1.0. Also, it is obvious that while the actual ROVAC COP's are quite good by current standards, they fall considerably short of the performance predicted by computer simulator. This data mismatch is discussed subsequently in a following section.

THE DODGE CORONET ROVAC AIR CONDITIONING SYSTEM - In April of 1973, Chrysler Corp. contracted with The ROVAC Corp. to produce an appraisal ROVAC automotive air conditioning system and install it on a Chrysler-supplied Dodge Coronet. Fig. 10 is a photograph of the ROVAC-Dodge installation.

In the Dodge system, air flows from either the car's interior or the outside into the circulator, a model 308/45/9.5-4 machine. After passing through the compressor section, the circulator air passes through the intercooler placed in front of the radiator and then re-enters the circulator on the expander side. After expansion, the cold air emerges into the car's existing ducting system through an insulated duct. This cold air then passes through the humidity control element where it subsequently is mixed with interior or exterior air and propelled through the existing air conditioning plenum and registers to the passengers via the existing heater fan. Condensed moisture leaves the automobile from the existing condensate drain.

Tests performed in Florida on the ROVAC-equipped Dodge Coronet yielded significantly positive results. The delivery of cold air to the passenger compartment was nearly instantaneous and more than adequate cooling capacity was quite apparent even at low road speeds under very hot and humid conditions. A typical jury test was performed after thermally soaking the automobile in 95°F ambient Florida sun for approximately three h wherein the interior car temperature rose to 105°F. Five adult passengers (including one Chrysler Engineer) entered the car and the windows remained closed. The Coronet was driven for approximately 10 min at 30 mph with windows closed and no fan air. The interior temperature of the car rose to 107°F and the system was engaged. Within one minute and 53 s, the interior temperature of the automobile dropped to 72°F. Engine speed averaged about 1300 rpm (approximately 30 mph) throughout the slow speed cooldown test. The idle condition cooling level was also judged to be fully adequate. Bearing in mind that the Dodge Coronet was the first automobile in history to be effectively air conditioned through the use of atmospheric air as the refrigerant, the prognosis for the future is promising.

GENERAL DISCUSSION: CONCLUSIONS AND RECOMMENDATIONS

The major problem area in the design and fabrication of ROVAC circulators is devising simple embodiments and techniques that minimize mechanical friction while simultaneously maximizing internal air sealing of the machine over a wide range of rotor speeds. This translates directly to three areas: 1. maximizing structural rigidity (especially the rotating components), 2. determining proper contour relations, and 3. dimensional tolerance.

As might be expected, therefore, during the construction of this machine, numerous fabrication problems were encountered, both in the non-rotating and rotating subcomponent areas. At the outset, the most obvious serious fabrication and difficulties were with the precision contouring of the stator and the alignment and concentricity of the cam profiles. After these problems were solved, attention was focused upon the fabrication of the rotating elements. The problems associated with this area consisted of maintaining good surface finish, true radial element rotor slots and axle-centered vanes. Techniques for fabricating these subcomponents were also developed which pave the way for mass production of the parts.

Once processes and techniques were developed which provided design-print hardware, the actual measured performance of the prototype systems was seen to be, by current comparisons with conventional automotive air conditioning systems, favorable. Nonetheless, the prototype systems' performance, considering the computer performance predictions, has a great margin for further improvement. Specifically, current automotive ROVAC performance is seen to be in the range of about 1.3 at high specific humidity ratios. It is predicted that this number can increase to the vicinity of 3.2; over three times that of conventional laboratory system performance.

The present approach to optimizing ROVAC performance is three-fold:

1. Instrumenting all internal Pressure-Volume and Temperature-Volume processes in order to determine precisely the actual port location requirements.
2. Further improvement of the mechanical design of all Circulator subcomponents.
3. Isolate and minimize adverse heat transfer.

The first area of improvement is very important; present port locations, while determined with a sophisticated computer program, cannot be expected to be completely accurate. This is due primarily to the fact that the physics and thermodynamics of the multi-mixed phase processes are modeled only on a simplified basis and that the actual cut-off point for port flow is not precisely determinable because of the vane tip contour.

The second area of improvement is also important and will entail the design of more rigid vanes and rotors and trimming in contours to account for thermally induced stator dimensional changes.

In addition to the direct mechanical alterations, attention is also being given to optimizing the thermal flow within the Circulator. Also, some activity has been directed towards port noise abatement. Preliminary development approaches have yielded large decreases in sound output. For example, the 306 and 308 circulators produce approximately 105 db (A-scale) at a distance of one foot without manifolds. Minor port modifications on the 209 circulator reduced the level to 85 db without manifolds. Due to this rewarding result, the port design will receive further attention. The goal for automotive circulator sound generation is 75 db without manifolds and 65 db with manifolds. Actual tests within the Dodge Coronet shows that no measurable sound is transferred to the interior of the car through the ducts. However, noise emanating from the manifolds in the engine compartment, reaches the passenger area from road reflection and the hood area. Measurements indicate that passenger area noise level with the 308 circulator is approximately 6-8 db above the ambient cruise noise level; obviously an unacceptable level. While a model 209 circulator has not been installed in an automobile by writing time, the low db output from this machine with manifolds indicates that noise levels, both by-pass and interior, would be fully acceptable by present standards.

The humidity control module, which is basically a simple filter element, has not seen long enough use to determine if a long-term clogging problem will eventually develop. From an optimistic viewpoint, however, there is a basis for belief that, due to condensation, the filter will be constantly washed. If this is not the case, periodic element replacement would be required.

The only material area that the ROVAC automotive system has not demonstrated absolute credibility is circulator longevity. Most test data on the later generation machines are based on individual operating runs of no more than 15 min. Total individual logged operating time on the third and fourth generation machines does not exceed 10 h. However, the second generation machine (Fig. 1) logged over 300 total hours without failure or notable wear. Naturally, due to the short operating times, no measurable wear has been noted on the latest machines.

In spite of the absense of long term reliability data at printing, there exists data and operating information on materials and machines operating under similar, and in some respects more severe, conditions. For example, "smog" pumps, dry rotary vane motors and dry rotary vane vacuum pumps, all operate at respectable speeds and under varying conditions. Dry operating rotary vane machines (with vane tips rubbing against the stator housing) are available off-the-shelf with guaranteed lifetimes of 4000 hours. These facts, coupled with design knowledge of the circulator materials, and existing test data builds a credible basis for expecting ROVAC machines to demonstrate quite favorable longevity.

In conclusion, the past development of the ROVAC system has demonstrated without question the capability of employing ordinary atmospheric air to serve as an exceptionally effective refrigerant for the air conditioning of automobiles. It now appears within sound judgement to anticipate the reality of the major contribution brought forth by the advent of ROVAC.

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APPENDIX C

PERSONS AND FIRMS CONTACTED

AIR CONDITIONING AND REFRIGERATION CONTACTS

1. Mr. Frank Vergasi
   Air Conditioning, Heating, and
   Refrigeration News
   Birmingham, Massachusetts

2. Mr. H. T. Gilkey
   Air Conditioning and
   Refrigeration Institute
   Arlington, Virginia

3. Mr. H. L. Noble
   Allied Chemicals Corporation
   Morristown, New Jersey

4. Mr. Louis Marz
   Amana Refrigeration
   Amana, Iowa

5. Mr. James Stevens
   Appliance
   Elmherst, Illinois

6. Mr. Arnold Consdorf
   Appliance Manufacturer
   Chicago, Illinois

7. Mr. R. J. Destiche
   Mr. John Hester
   Arkla Industries
   Little Rock, Arkansas

8. Mr. Roger Shamel
   Mr. R. Williams
   Mr. Robert Green
   Arthur D. Little, Inc.
   Cambridge, Massachusetts

9. Mr. Herb Phillips
   Association of Home Appliance
   Manufacturers
   Chicago, Illinois

10. Mr. Ben Wilson
    Bahnson Company
    Winston-Salem, North Carolina

11. Mr. Huddleson
    Mr. David Wilson
    Carrier Corporation
    Columbus, Ohio

12. Mr. James Holtslag
    Chrysler Corporation
    Detroit, Michigan

13. Mr. John Knoble
    Croll-Reynolds Company
    Westfield, New Hersey

14. Mr. Jerry Fortier
    Cryogenic Technology, Inc.
    Waltham, Massachusetts

15. Dr. Hans Borchardt
    Mr. Clark Hoffman
    Du Pont Freon® Products Laboratory
    Wilmington, Delaware

16. Mr. Billy Owens
    Federal Energy Administration
    Washington, D.C.

17. Mr. Gerald Stofflet
    Mr. J. A. Dobb
    General Motors Corporation
    Warren, Michigan

18. Mr. Todd Merrill
    International Mobile Air
    Conditioning Association
    Dallas, Texas

19. Mr. Milton Levine
Melcor Materials Electronic
  Products
Trenton, New Jersey

20. Mr. Ciricillo
Ranko Corporation
Columbus, Ohio

21. Dr. Thomas Edwards
Rovac Corporation
Maitland, Florida

22. Mr. H. L. Munde
Mr. R. L. Maier
Southwest Factories, Inc.
Oklahoma City, Oklahoma

23. Mr. J. V. Weigle
Mr. R. D. Randall
Dr. K. S. Sanvordenker
Tecumseh Products Company
Tecumseh, Michigan

24. Trane Company
La Crosse, Wisconsin

25. Dr. Lawrence Midolo
United States Air Force
  Flight Dynamics Laboratory
WPAFB, Dayton, Ohio

26. Mr. J. McLean
Westinghouse Corporation
Columbus, Ohio

27. Dr. Gale Cutler, et al.
Whirlpool Corporation
Benton Harbor, Michigan

28. Mr. W. T. Ferguson
York Division of Borg-Warner
York, Pennsylvania

AEROSOL INDUSTRY

1. Mr. Bob Tucker
President
Container Division
Plant Industries, Inc.
Montreal, Canada

2. Mr. Donald Knox
Calmar Division
Diamond International Corporation
New York, New York

3. Mr. Dan Massey
Marketing Manager
Valve Corporation of America
Baton Rouge, Louisiana

4. Mr. Frederick Muller
Executive Vice President
Bakan Plastics Division
Realex Corporation
Kansas City, Missouri

5. Mr. Hal Goldman
Marketing Research Manager
The Mennon Company
Morristown, New Jersey

6. Mr. Pat Adamo
Division of Regulatory Guidelines
Bureau of Foods
Food and Drug Administration
Washington, D.C.

7. Mr. Charles S. Hayes
Applications Engineer
Chemetron Corporation
Chicago, Illinois

8. Mr. Edward Kalat
Research and Development
Aerosol Packaging Component Division
Risdon Manufacturing Company
Thomaston, Connecticut

9. Amway Products
Distribution Center
Kansas City, Missouri

10. Mr. Charles S. Booz, Jr.
Public Affairs Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware

11. Mr. John C. Bray (and others)
Market and Product Development Manager
Aerosol Propellants
Freon® Products Division
E. I. du Pont de Nemours and Company
Wilmington, Delaware

DEGREASING AND DRY-CLEANING

1. Mr. Francis Figiel
   Technical Specialist
   Technical Service
   Specialty Chemicals Division
   Allied Chemical Corporation
   Morristown, New Jersey

2. Mr. Robert Orseo
   Allied Chemical Corporation
   Buffalo, New York

3. Mr. Ralph Dermott
   American Society of Metals
   Metals Information Department
   Metals Park, Ohio

4. Mr. Anderson
   Anderson Myers Company, Inc.
   Kansas City, Missouri

5. Mr. Arthur
   Baron Blakeslee
   Vapor and Ultrasonic Degreasers
   Cicero, Illinois

6. Mr. Geroald Gershon
   Chemical Commodities Inc.
   Olathe, Kansas

7. Mr. T. Kearney
   Senior Engineer
   Mr. George Leith
   Manager, Special Products Sales
   Detrex Chemical Industries, Inc.
   Detroit Michigan

8. Mr. Ken S. Suprendnt
   Chlorinated Solvents
   Dow Chemical, USA
   Midland, Michigan

9. Mr. Curt O'Hogan
   Dow Chemical, USA
   Johnson County, Kansas

10. Mr. Maltman
    Solvent Section
    E. I. du Pont de Nemours and
    Company, Inc.
    Wilmington, Delaware

11. Mr. Bill Fisher
    Joliet, Illinois
    Mr. Lloyd
    Silver Spring, Maryland
    International Fabricare

12. Livingston Industries, Inc.
    Lenexa, Kansas

13. Mr. Ishmial Akbay
    Mr. Mack Sharp, NASA
    George C. Marshall
    Space Flight Center, Alabama

14. Missouri Solvents and Chemicals
    Kansas City, Missouri

15. Solvent Supply Company
    Kansas City, Missouri

16. Mr. Tom McDonald
    Vic Manufacturing Company
    Minneapolis, Minnesota

FOAM BLOWING INDUSTRY

1. Mr. H. Lee Noble
   Allied Chemical Company
   Morristown, New Jersey

2. Mr. Joseph Hope
   Allied Chemical Company
   Director of Fluorocarbon Marketing

3. Mr. Ken Meinert
   Manager, Corofoam Division
   Cook Paint and Varnish Company
   North Kansas City, Missouri

4. Mr. Tom Morriss
   Corofoam Division
   Cook Paint and Varnish Company
   North Kansas City, Missouri

5. Dr. Charles F. Kloss
   Uniroyal, Inc.
   Naugatuck, Connecticut

6. Mr. Richard B. Ward
   Freon Products Laboratory
   E. I. du pont de Nemours
   Wilmington, Delaware

7. Mr. Arthur Chivas
   Executive Director, Urethane Safety Group
   SPI
   New York

8. Mr. McLaughlin
   SPI
   New York